Published Monthly. Price, $5.00 per Annum.

THE JOURNAL
OF THE
AMERICAN CHEMICAL SOCIETY.

VOL. XVII.—NO. 11.

NOVEMBER, 1895.

EDWARD HART, Editor, J. H. LONG, THOMAS B. OSBORNE.
COMMITTEE ON PAPERS AND PUBLICATIONS.

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CHEMICAL PUBLISHING COMPANY.

Entered at the Post Office, Easton, Pa., as Second Class Matter.

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PAPERS ACCEPTED FOR PUBLICATION:

The Determination of Methane and Hydrogen by Exposition. By Augustus H. Gill.
On the Estimation of Levulose in Honeys and Other Substances. By H. W. Wiley.
On the Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali. By B. W. Kilgore.
Estimation of Phosphoric Acid in Soils by Double Precipitation with Molybdic Solution and Titration of the Ammonium Phosphomolybdate with Standard Alkali. By C. B. Williams.
The Determination of Phosphoric Acid by the Molybdate-Magnesia Method and by Volumetric Method. By B. W. Kilgore.
The Relationship of the Heat of Vaporization of Gases to their Density, and also to their Boiling-Point. By Wm. L. Dudley.
Heats of Solution of some Carbon Compounds. By C. L. Speyer.
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An Improved Gas Pipette for the Absorption of Illuminants. By Augustus H. Gill.

Issued with November Number, 1895.

Proceedings.

NEW MEMBERS ELECTED OCT. 10.

Browne, Arthur Benjamin, 119 Water St., Boston, Mass.
Burt, M. C., Amherst, Mass.
Chamberlain, Geo. D., care of Iroquois Furnace, S. Chicago, Ill.
Johnson, Edward S., Park Bros. & Co. Steel Works, 33d and Smallman Sts., Pittsburgh, Pa.
Lindsey, J. B., Ph.D., Expt. Station, Amherst, Mass.
Louderbeck, Harry C., Griffin Wheel Co., Chicago, Ill.
Lovejoy, Ellis, Union Furnace, Ohio.
McCrae, John, Ph.D., Univ. of Cincinnati, Cincinnati, Ohio.
Noyes, Dr. Arthur A., Mass. Inst. of Tech., Boston, Mass.
Sanborn, E. R., Sharon, Pa.
Taylor, Edward R., S. B., Cleveland, Ohio.
Underwood, Edward L., Canton, Mass.
Wakeman, Alfred J., 819 Madison Ave., N. Y. City.
Withers, W. A., Raleigh, N. C.

CHANGES OF ADDRESS.

Couch, Guy E., Pottsville, Pa.
Drown, Thomas M., South Bethlehem, Pa.
Fuller, Geo. W., Box 614, Louisville, Ky.
Hornbeck, S. L., Tehuacana, Texas.
Linn, Prof. A. F., Wittenberg College, Springfield, O.
Moale, Philip R., care of N. Y. and Boston Dyewood Co., Green and West Sts., Greenpoint, Brooklyn, N. Y.
Nicholson, Edward E., 716 University Ave., S. E., Minneapolis, Minn.
Pearce, Edward D., care of T. P. Shepard & Co., Box 1336, Providence, R. I.
Sherman, H. C., 252 W. 53d St., New York City.

MEETINGS OF THE SECTIONS.

LEHIGH VALLEY SECTION.

The Fall meeting of the Lehigh Valley Section was held at Bethlehem, October 10. Thos. Tyrer, President of the Society of Chemical Industry of England, was the guest of the Section,

and he was accompanied from New York by representatives of the New York Section of the Society of Chemical Industry and the New York Section of the American Chemical Society, in a parlor car, kindly provided by the Lehigh Valley Railroad. It had been hoped that Ludwig Mond, F. R. S., who accompanied Mr. Tyrer to America, would also be present, but he was prevented by business engagements.

Reaching Bethlehem at 10.30 A. M., the party inspected the works of the Bethlehem Iron Co., and the officials took them through every department of the government plant. After visiting the laboratory, which through the labors of Albert L. Colby, formerly chemist, now metallurgical engineer, and C. A. Buck, chief chemist, is probably the best equipped in its facilities for doing rapid work of any in the country. The company provided their guests with a dinner served in the works offices, to which forty-two sat down.

The stated meeting was held at 4.30 P. M., Prof. Edward Hart, presiding officer in the chair.

Albert L. Colby read a paper on the "Rapid Methods perfected in the Laboratory of the Bethlehem Iron Co., and in Use There." At the close, he presented each member with a novel souvenir, a nickel-plated armor plate washer manufactured by the company, on which was stamped the date and place of meeting of the Section and the name of the person to whom it was presented. In the centre was engraved, "Accurately analyzed for carbon in 12 minutes, Manganese in 10 minutes, Phosphorus and Silicon in 30 minutes."

Other papers were read as follows: "Chemical vs. Bacteriological Examination of Water." Prof. Wm. P. Mason, of Troy, read by Dr. Wm. McMurtrie. "On Standardization of Iodine Solution," by G. H. Meeker." "A Device for Sampling Metals," by Porter W. Shimer."

Following the reading of papers, interesting responses were made by Thos. Tyrer, Esq., Alfred Mason, and Peter T. Austen. The New York delegation made the return trip at 6.30 P. M., and the meeting was voted to be the most successful one in the history of the Section.

ALBERT H. WELLES, Secretary.

CINCINNATI SECTION.

A meeting of the Cincinnati Section was held on October 15.

Dr. Alfred Springer presented "A Tribute to Pasteur," and papers were read on "The Laboratory Uses of Aluminum" and "Recent Progress in Theoretical Chemistry" by Prof. T. H. Norton.

Dr. John McCrae, instructor in chemistry, University of Cincinnati, and Prof. A. F. Linn, professor of chemistry, Wittenberg College, Springfield, O., were elected members of the Section.

RHODE ISLAND SECTION.

A meeting of the Rhode Island Section was held at Providence on Thursday evening, Oct. 17, 1895, Chairman C. A. Catlin, presiding.

Dr. H. J. Wheeler, of the Rhode Island Agricultural Experiment Station, read a paper upon "Acidity of Soils and its Relation to the Growth of Agricultural Plants and to the Development of the Potato Scab."

Attention was called to the fact that though the mention of sour soils appears to be almost universal, it is but rarely that any writer on agricultural chemistry has called attention to the fact that upland, light, and naturally well-drained soils are ever so acid as to be injurious to the growth of plants, and then generally, only where acidity was concluded. Instances of the occurrence of a degree of acidity in soils of this character sufficient to be injurions to many agricultural plants were cited from places in Massachusetts, Maryland, and Kingston, West Kingston, Westerly and Hope Valley, R. I. Acidity apparently of an equal degree, has been observed in many other places in New England where the effect of the same has not yet been established by actual experiments. In the course of the experiments at the R. I. Agricultural Experiment Station, covering a period of three years, over ninety varieties of plants have already been employed. The most marked differences in the effect of acid soils before and after liming have been observed in connection with plants which have ordinarily been grouped as requiring similar soil and fertilization. Photographs were shown illustrating that the presence of carbonates or the existence of acidity in soils has a wonderful

effect upon the development on potato tubers of the bacterioid fungus which causes the potato scab. The necessity for acid tests in soils of the above-mentioned character, particularly when derived from certain granites and mica schists, was strongly emphasized.

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AN ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF WHITE LEAD.[1]

BY R. P. WILLIAMS.

Received September 9, 1895.

WHITE LEAD is the basis *par excellence* of white paint. For hundreds of years it has been used, mixed with linseed oil, as the main pigment where permanent, opaque, white color is desired.

Up to the present time there have been but two radically different processes of manufacture that have proved in any degree successful. These are known as the Dutch and the French processes. The English and the German are only modifications of the same principle as the others. The Dutch process is the only really successful one. I do not propose to go into the details of either of these processes, since they are well known to every chemist, but only to recall just enough of them to serve as the basis of comparison and as an introduction to the one I am to describe. Both the French and the Dutch, as well as the many modifications of them, depend upon one compound; *viz.*, lead acetate (or better, sub-acetate). This is the compound which has always been regarded as the essential first step in white lead manufacture. The fact is interesting, since white lead as a pigment has been known for more than 2,000 years, and from the earliest times it has been made by the action of acetic acid on lead. The name, Dutch process, is a

[1] Read at the Springfield meeting.

misnomer, as the process was introduced by the Dutch or Flemish people over 300 years ago from Italy, where it had been employed for hundreds of years previously. In fact, Pliny in the first century describes the essentials of the process, and it is said to have been employed in his country ever since his time, though, of course, on an extremely limited scale at first. Indeed Theophrastus, about 300 B. C., describes the preparation of a white pigment from lead and vinegar. This may have been the acetate, or it may have been the carbonate. The new process is a radical departure from all the old ones in not employing acetic acid at all, but in acting upon lead with nitric acid, which is generated by electricity.

The process consists of four reactions, as given below. First, the electrical preparation of nitric acid and sodium hydroxide. Second, the action of the nitric acid on lead, forming lead nitrate. Third, the reaction of lead nitrate and sodium hydroxide to form lead hydroxide. Fourth, the combination of lead hydroxide and sodium bicarbonate to form lead carbonate.

In the first step of the process, a solution of sodium nitrate is decomposed by an electric current from a dynamo. The strength of solution required is not important, 10° Baumé, or say one pound to the gallon, being sufficient. This solution is put into a series of cells, constructed of wood, and divided into two compartments by a porous partition. At the plus electrode is fastened a pig of lead, and at the minus a sheet of copper. The solution being run in from an overhead reservoir, and the current turned on, the nitrate is decomposed according to equation (1), nitric acid collecting at the plus electrode and sodium hydroxide at the minus. The nitric acid at once attacks the lead and forms lead nitrate, which dissolves, equation (2), whereas the sodium hydroxide produces no effect on the copper at the negative pole. Finally the lead nitrate solution and the sodium hydroxide solution are drawn off separately, and mixed as desired, in quantitative proportions, in a receptacle. The result as shown in equation (3), gives lead hydroxide as a white, amorphous precipitate, and leaves sodium nitrate in solution. This is practically the original nitrate, and its regeneration shows one of the economic excellencies of the

process, for the nitrate can be used over and over again, as the source of more acid.

It has been found at the experiment station, that but little additional sodium nitrate is required for a repetition of the process as complete as the original. The lead hydroxide is then filtered from the sodium nitrate. This is done automatically and continuously, by a rotary filtering device, and the sodium nitrate is pumped back into the original reservoir. The fourth step is, in some respects, the most interesting of all, and consists in adding to the lead hydroxide a solution of sodium bicarbonate (or of the normal carbonate). Reaction (4) at once takes place. It will be noted that sodium hydroxide is the product in solution, and lead carbonate the precipitate. Another beauty of this process is that the sodium hydroxide removes most of the impurities, if there are any, in the lead hydroxide; for instance, it will dissolve any salts of aluminum or of zinc, and it removes organic matter.

These impurities appear in the solution, leaving the precipitate remarkably white. Once more, this by-product, sodium hydroxide, by passing carbon dioxide into it, is converted into bicarbonate and the latter can be used again. Thus the main agent in each of the two principal steps, sodium nitrate and sodium bicarbonate, is made to do duty over and over again, with but slight additions.

(1) $NaNO_3 + H_2O = \overset{-}{Na}OH + H\overset{+}{N}O_3$.
(2) $2HNO_3 + Pb = Pb(NO_3)_2 + H_2$.
(3) $Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$.
(4) $Pb(OH)_2 + HNaCO_3 = PbCO_3 + NaOH + H_2O$.

It is doubtful whether (1) and (2) take place as above, but probably the reaction is as follows, since hydrogen is liberated at the minus electrode:

$$2NaNO_3 + 2H_2O + Pb = (2\overset{-}{Na}OH + H_2) + Pb\overset{+}{O}_2(NO_2)_2.$$

Let us now turn from the theoretical to the practical part of the matter. The first question which naturally arises is, will this process so beautiful in theory, and as a laboratory experiment, work on a large scale and give sufficiently practical

results to compete with the other methods of manufacture, and make it a lasting contribution to inventive science?

An experimental station was for several months in operation in Cambridge, Mass., erected and run under the direction of Mr. Arthur Benjamin Brown, the inventor of the process. This was capable of turning out some 500 pounds of white lead per day. Its success was regarded as beyond question. The cost of white lead by this process is more than covered by the gain in weight, and is but a fraction of the cost by the Dutch method. The reasons are, first, in the electrolytic process pig lead is used, as it comes from the smelting furnace. In the Dutch it has to be remelted, cast into "buckles" of definite size, and, after the action of acetic acid, from one-third to one-half is left uncorroded and has to be recast.

Second, the process is almost instantaneous, as every reaction takes place rapidly, while by the other mode from two to six months is required.

Third, in materials and labor there is great saving. No free acid is used, either acetic or nitric, and the agents sodium nitrate and bicarbonate, are used repeatedly. By the old method a plant covering a large area is filled for months with fermenting tan bark or manure, acetic acid and lead, while the process is going on, and at its completion, the product is removed with much labor, and has to be thoroughly and repeatedly washed to dissolve out any lead acetate remaining. It must be ground and reground under water, and even then is not likely to be of uniform texture. It is also a poisonous and dirty process. The electric method being continuous, is complete the same day, requires but a very small force of men, as almost all the operations are automatic, and is a clean and non-poisonous process.

The texture of the product is almost molecular in fineness, as might be expected from its being produced by replacement in the hydroxide. Hence it needs no grinding. It is so fine as to remain suspended in water for a long time, and in order to filter it a special brand of cloth had to be made, as even filter-paper would scarcely retain it.

One of the most important practical questions is: How does

paint made from electrolytic white lead compare with that made from Dutch lead in durability, opacity, and covering power? Specimens have been submitted to some of the largest dealers and painters in New England and elsewhere, and Mr. Brown, the inventor, has spent the last two years, aided by a competent corps of assistants, not only in the development of his new process, but in making thorough and systematic tests of the product. Inside and outside surfaces have been exposed to the severest extremes of weather, to the varied fumes of the laboratory, and to other crucial tests. Dutch paint and electrolytic paint have been exposed side by side for two years, and no difference can be detected in durability or opacity. The covering power of the new paint is considerably greater than that of the Dutch. Experiments vary as to the increased percentage from twelve to twenty, or even higher, but in no case was there found to be a smaller percentage.

What is the cause of such an increase? This leads us to discuss somewhat more fully the nature and composition of white lead made by the various processes. Dutch white lead consists approximately of two molecules of the carbonate to one of the hydroxide, $2PbCO_3.Pb(OH)_2$. This, however, appears not to be constant, as might be inferred from its mode of manufacture. Lead hydroxide is a white, amorphous substance. Lead carbonate is either a spongy transparent, globular powder, or is crystalline. Whether globular or crystalline depends upon its mode of preparation. Now certain properties of these two forms are quite different, and this difference explains the use of one and the disuse of the other form as a pigment. The globules of the one form are said to be from 0.00001 to 0.00004 of an inch in diameter. These, in the grinding of lead with linseed oil, are supposed to take up the oil, somewhat as a sponge absorbs water. The Dutch process lead is the globular variety, and to this fact has been attributed the greater body and permanence of the paint made from it than that made by most other processes. The crystalline variety of the carbonate is found not to absorb oil to anything like the same extent as the globular, no matter to what degree of fineness it is ground, the surface of the minute crystals being impervious. Half a century ago Thenard

invented the "quick process lead," or "French process." This is now carried on in Clichy, France, and some other places, and sold as "Clichy White." It is made by dissolving litharge in acetic acid and then passing into the sub-acetate of lead solution formed, carbonic acid gas. Thus is formed neutral lead carbonate. It was at first thought to be a revolutionary process, but it soon became apparent that the product did not give the capacity or body, which Dutch lead gave, and of course it lacked permanence. Made in this way the carbonate is crystalline. Under the brush it is found not to cover as much surface and not to spread as well, or it is said to lack "body," although of the same composition as the other. Other rapid processes—and there have been hosts of them—have invariably met with no better success, for the reason that the carbonate formed is the crystalline instead of the globular variety. To this fact we may mainly attribute the long continued use of Dutch process lead. The committee of experts appointed by the British Home Secretary, visited forty-six works, and found only one using the precipitation process, and three the chamber process. They say: "While some of the substitutes are cheaper to make, and far less poisonous, yet they are far from equalling the Dutch lead as a pigment. Neither can they recommend other process than the old Dutch process, for manufacturing the product."

Thus we see that until now, no cheaper method has been found for producing the globular variety. The electrolytic process *does* produce the globular kind, and a finer variety even than the Dutch, so fine in fact, that it was almost impossible to find a filter that would retain it. This probably accounts for the superiority of the electrolytic brand, as regards body and covering power over any other kind produced. Experiment shows that the pure carbonate will do as well as a mixture of carbonate and hydroxide. By the new process it is easy to make either the pure carbonate, or a mixture in any proportion, of carbonate and hydroxide. The practicability and cheapness of the electrolytic process, and the efficiency of the product being conceded, we may inquire lastly: What are the probabilities of this method being superseded by others in the future?

No other white pigment has yet been formed, or seems likely to be found, which will take the place of white lead. The two main substitutes are zinc white, ZnO, and permanent white, $BaSO_4$. But these do not stand the test with lead white, having far less capacity, and less covering power. Especially will they not compete with the cheapening of the latter by the new process. Hence, we must look to lead to give us the white pigment of the future.

Now what are the possible ways of making lead carbonate? There are but three common solvents of the metal; chlorine, acetic acid, nitric acid. Chlorine is at once ruled out for all practical purposes, for reasons that need not be mentioned here. Acetic acid seems to have been the substance universally employed to the present time, for getting the metals into a preliminary state for making the carbonate. As before noted, from the time of Theophrastus to the present day a host of persons in every age and many countries, have experimented and written upon the subject, all using the same method so far as concerns making lead acetate.

The inventor of the present process, worked a long time upon the acetate, but as acetic acid is an organic substance of quite complex structure, it broke up very readily under influence of an electric current, giving rise to unendurable fumes, and its use had to be abandoned. For these reasons it is safe to say that no electrolytic process is likely to employ the lead acetates. The only solvent left is therefore nitric acid. Free nitric is not likely to be used for three reasons: First, it could hardly be employed in electrolysis; Second, it would be more expensive than Chile saltpeter; Third, its reaction with lead would give rise to noxious nitric oxide fumes, and its by-product would not be re-usable. It should be said that no gases except hydrogen arise in the electrolytic process, in which the acid, as fast as liberated, combines with the lead, as may be seen from equation (2).

Now the only feasible source of nitric acid yet found, is either sodium or potassium nitrate. The former being far the more abundant and cheaper, is here as elsewhere employed, as a source of the acid, and no other nitrates are found to any extent in nature.

It would seem from what has been set forth, that not only is the process above described the most valuable and revolutionary ever invented for the manufacture of white lead, but that there is not a probability of any other process taking its place, in the near future.

This new process was invented in 1892, by Arthur Benjamin Brown, a chemist and mining engineer of Boston. It is to-day for the first time made public. The reason this has not before been done is because time was necessary to complete many details for production on a large scale, and to secure requisite patents. These are now completed, and a large company is organized to put the process into practical operation. I propose for this invention the name—The Brown Electrolytic Process.

THE CHLORIDES OF ZIRCONIUM.[1]

By F. P. VENABLE.

Received September 9, 1895.

IN a report upon the examination of the chlorides of zirconium[2] it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann[3] the result of which made him call the substance the tetrachloride ; and on repeated partial analyses of my own in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey) 39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being

[1] Read at the Springfield meeting.

[2] *J. Am. Chem. Soc.*, *1894*, 16, 460–475.

[3] Lond. Chem. News, 52, 233–240.

unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition along with its stability would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is $Zr_3(OH)_5Cl_7.5H_2O$.

UNIVERSITY OF NORTH CAROLINA,
August, 1895.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. No. 7.]

THE DETERMINATION OF THE HEATING EFFECTS OF COALS.[1]

BY W. A. NOYES, J. R. MCTAGGART, and H. W. CRAVER.[2]

Received September 9, 1895.

MANY determinations have been made for the purpose of comparing the heating effect of coals as determined by the calorimeter with that calculated from analyses. Scheurer-Kestner, who seems to have been the first to show that the results obtained in the two ways do not agree, publishes results obtained with the calorimeter of Favre and Silbermann, which differ, in some cases, by ten per cent. from those calculated by Dulong's formula and are uniformly higher.[3] In a later paper[4] he states that he finds lower results with Bertholet's bomb but still results that differ from those calculated.

[1] Read at the Springfield meeting.

[2] The work of which this paper gives an account formed the basis of theses presented to the faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science.

[3] *Compt. rend.*, 106, 1092, 1160, 1230.

[4] *Ibid*, 112, 233.

Ferd. Fischer claims repeatedly in the *Zeitschrift für angewandte Chemie* and elsewhere that the calorimeter results differ from the calculated heating effect, but admits that the latter may answer for most technical purposes.

Hempel[1] states that the results calculated from careful analyses do not differ more than one or two per cent. from those of the calorimeter and considers that larger differences sometimes found have been due to careless work. He gives six cases of fair agreement, but one which shows a difference of six per cent.

Alexejew[2] gives one case in which the calorimeter result is three and eight-tenths per cent. higher than that calculated.

Scheurer–Kestner[3] has compared the results obtained with Thompson's calorimeter (burning with potassium nitrate and potassium chlorate) with those given by the calorimeter of Favre and Silbermann and finds a maximum difference of three and a half per cent. In using Thompson's method, however, he applies a constant plus correction of fifteen per cent., which F. Fischer criticises as very unreliable.

W. Thompson[4] describes a simple calorimeter which he has devised and gives results obtained with twelve samples of coal. In seven cases the results are lower, in two cases they are the same, and in three cases they are higher than those calculated. F. Fischer[5] criticises these results, saying that the coals were probably not completely burned.

Barrus has described[6] a calorimeter which he appears to have copied from that of W. Thompson.

C. v. John and H. B. Fuller[7] have made a series of comparisons of Berthier's test (reduction of litharge) with the results calculated from analyses. The latter give, in some cases, 900 calories more than the former.

So far as we are aware, no comparisons of this kind have been made with American coals. The work here described was un-

1 *Ztschr. angew. Chem.*, *1892*, 393.
2 *Ber. d. Chem. Ges.*, **19**, 1557.
3 *Compt. rend.*, **106**, 941.
4 *J. Soc. Chem. Ind.*, **5**, 581, and **8**, 525.
5 Jahrb. chem. Tech., *1889*, 9.
6 Trans. Mech. Eng., **14**, 816.
7 *Ztschr. angew. Chem.*, *1893*, 285.

dertaken for the purpose of comparing the results obtained with Hempel's calorimeter with those calculated from analyses and those obtained by Berthier's test. Six specimens of representative Indiana coals were used, as follows: Brazil Block from Brazil, Lancaster Block from Clay Co., Shelburn coal from Shelburn, two samples from the mines of the New Pittsburg Coal Co. at Alum Cave, and a sample of mine screenings used in the shops of the Rose Polytechnic Institute. The first two are known locally as "block" coals and are non-coking. The others are known as bituminous and are coking coals.

ANALYSES.

The analyses were made as follows:

1. *Moisture.*—One gram of the coal was dried in a toluene-bath (about 105°) for one hour.

2. *Ash.*—The residue of (1) was ignited over a Bunsen burner, at first with a very low flame, till the carbon was completely burned.

3. *Fixed Carbon.*—One gram of fresh coal was placed in a covered platinum crucible and heated with the full flame of a Bunsen burner for just seven minutes. The residue less the ash is the "fixed carbon."

4. *Volatile Combustible Matter.*—The loss of weight in (3) less the moisture is volatile combustible matter.

The above determinations are, of course, of no value for the calculation of the heating effect but give some indication of the character of the coal.

5. *Carbon and Hydrogen.*—About two-tenths gram of the coal was burned in a current of oxygen in a hard glass tube containing copper oxide and lead chromate.

6. *Nitrogen.*—This was determined with soda-lime.

7. *Sulphur.*—Determinations were made by Eschka's method, using potassium carbonate and magnesium oxide, by the method of Carius and by the use of sodium peroxide, as follows: one-half gram of the coal was weighed out in a platinum dish holding about fifty cc. and three grams of sodium peroxide and a little water were added. The whole was evaporated to dryness and ignited. After adding two grams of sodium peroxide and more water the evaporation and ignition were repeated. The mass was then

boiled with water, the solution filtered, acidified, and precipitated as usual. The barium sulphate was purified by fusion with sodium carbonate. The results obtained by this method agreed fairly well with those obtained by Eschka's method, but the results of Carius' method were mostly higher. As a comparison of methods was not part of our plan, the average of the results obtained by Eschka's method are given in the table.

8. *Oxygen.*—In most coal analyses the oxygen has been calculated by subtracting the other constituents, including the ash, from 100. Where the sulphur is low this introduces but a slight error. But with sulphur so high as in some of these coals the error is quite appreciable. The sulphur is mostly present in the form of pyrites and it has been assumed that this is burned to sulphur dioxide and ferric oxide. Accordingly, for the calculation of the oxygen, a correction has been applied to the ash by adding to it five-eights of the weight of the sulphur present.

The quantities given in the following table are in every case, the average of at least two results obtained by different persons. Where the agreement was not fairly close, a larger number of determinations has been made, and results differing too far from the mean have been rejected. For the results finally used, the average variation from the mean is 0.08 per cent. for carbon, and 0.18 per cent. for hydrogen. These differences correspond to a difference of fifty-seven calories, or about nine-tenths per cent. of the calculated heating effect.

The heating effect is calculated for the coal burned to vapor of water by the formula $8080C + 28800(H - \frac{1}{8}O) + 1582Fe + 2162S$, where C, Fe, etc., are the amounts of each element present. As will be seen from the table, the heating effect of the iron and sulphur is quite important in some of these coals.

CALORIMETRIC DETERMINATIONS.

The calorimeter used was that described by Hempel.[1] The powdered coal was compressed into cylinders, through which a fine iron wire passed. This wire was weighed, and it was assumed that it gave one-fifth as much heat by its combustion, as the same weight of coal. The autoclave was filled with oxy-

[1] *Ztschr. angew. Chem.*, *1892*, 393. See also Hempel's Gas Analysis, translated by L. M. Dennis.

gen, by generating the gas from a mixture of potassium chlorate and manganese dioxide. The temperatures were read by means of a telescope, the thermometer being graduated into fifths. The highest point reached by the thermometer, was used for the calculation. As the rise in temperature was only about five degrees, and the same method was used in determining the water equivalent of the calorimeter, the error due to radiation must have been small. The water used was delivered from a measuring flask, and was found by direct weight to be 997.8 grams. The water equivalent of the autoclave and calorimeter was determined by burning pure sugar charcoal as directed by Hempel. Six determinations gave an average value for the whole, including the water used of 1337.5 grams, with a probable error of five and nine-tenths grams or 0.45 per cent.

At least three determinations were made with each coal. The average difference of the values obtained from the mean for a given coal, was thirty-two calories, or one-half per cent.

The water formed by the combustion in the calorimeter condenses, of course, to liquid water, and, assuming that the average temperature of the calorimeter is 26°, a correction of 610 calories per gram of water formed must be subtracted to find the heating effect when burned to vapor of water. The results given in the table have been corrected in this manner.

BERTHIER'S TEST.

This was made as follows: One gram of the coal was intimately mixed with forty grams of litharge and the mixture put in a Battersea C crucible, seven and a half cm. deep, and four and a half cm. internal diameter, and covered with a layer of salt. The covered crucible was then placed in a *hot* gas furnace and heated for fifteen or twenty minutes. The crucible was then taken out, tapped to collect the lead, cooled, broken, and the lead button cleaned and weighed.

Theoretically, one gram of lead should correspond to a heating effect in the coal of 234 calories. The results calculated with this factor are, however, about twelve per cent. too low. The average of the results obtained, give an empirical factor of 268.3 calories per gram of lead. The results given in the table have been calculated with this empirical factor.

At least three fairly concordant determinations were obtained for each coal. A few results differing from this mean by more than one-half a gram of lead were rejected. The average difference of the results from the mean for a given coal, was 0.11 gram, which corresponds to twenty-nine calories or about 0.45 per cent.

The following table gives the results of the analyses and other determinations. The differences between the other determinations and those made with the calorimeter are given in per cents.

	New Pittsburg *A.*	New Pittsburg *B.*	Lancaster.	Brazil.	Shelburn.	Shop.
Moisture	6.83	5.89	12.66	8.98	8.63	2.36
Volatile combustible matter	39.92	42.23	37.44	34.49	38.82	31.11
Fixed carbon	39.93	40.40	47.22	50.30	43.45	42.44
Ash	13.31	11.48	2.68	6.23	9.05	24.09
Carbon	62.88	65.26	71.41	70.50	66.86	57.32
Hydrogen	5.07	5.17	5.56	4.76	5.30	4.56
Nitrogen	1.01	1.17	1.54	1.36	1.50	1.44
Oxygen	13.06	13.25	18.42	16.29	15.69	9.93
Ash (corrected)	17.98	15.15	3.07	7.09	10.65	26.75
Sulphur	7.46	5.88	0.62	1.39	2.57	4.25
Iron, calculated	6.53	5.14	0.54	1.22	2.25	3.72
Calories per gram, calc'ted C	5081.	5272.	5770.	5696.	5402.	4632.
" " " " H	991.	1011.	939.	784.	962.	956.
" " " " S	161.	127.	13.	30.	55.	92.
" " " " Fe	103.	81.	9.	19.	36.	59.
Total	6336.	6491.	6731.	6529.	6455.	5739.
Difference, per cent	+2.6	+1.2	+0.4	—4.6	—1.2	—1.2
Calories per gram, Berthier's test, factor 268.3	6307.	6471.	6831.	6689.	6461.	5726.
Difference, per cent	+2.1	+0.9	+1.9	—2.3	—1.1	—1.4
Calories per gram, calorimeter	6175.	6415.	6703.	6846.	6532.	5806.

In discussing the results, it is worth while to notice that, so far as indicated by the agreement of duplicate determinations, about the same degree of uncertainty attaches to the calorimetric determinations and to the litharge test, while the uncertainty of the analysis is about twice as great. It is noticeable that the results calculated from the analyses, and those given by

Berthier's test, agree better with each other than either agree with the calorimeter results.

On the average Berthier's test, when the empirical factor is used, appears to be more reliable than the results calculated from the analyses.

While the differences between the results obtained by different methods are not very great, they are certainly greater than can be accounted for by the errors of the work. In the case of two of the most important coals, the Lancaster and Brazil black, the relative value of the coals as given by the calorimeter, is reversed as given by the analyses and by Berthier's test. There can be little doubt that the calorimeter gives most accurately the relative heating value of these coals.

Attempts to make determinations with anthracite coals were unsuccessful, because it was found impossible to compress it into cylinders, and we have not yet been able to burn it in the form of a powder.

Some attempts have also been made to use the calorimeter of Barrus,[1] but a deposit of carbon was always formed, and the results appeared to be entirely unreliable. It is probable that the results would be more satisfactory with anthracite coals.

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TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES WITH NOTES ON SOME NEW REACTIONS.[2]

BY CABELL WHITEHEAD.

Received Sept. 9, 1895.

TELLURIUM which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent, that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade

[1] Trans. Mech. Eng., 14, 816. See als W. Thompson, *loc. cit.*

[2] Read at the Springfield meeting

telluride ores, is a problem which, up to the present time, has baffled the skill of the metallurgists of the world. A few of the difficulties may be mentioned as follows: Tellurides do not give up their gold to mercury, cyanide or chlorine, they concentrate badly, a large percentage of the value being lost as slimes. They are difficult to roast, on account of their low melting-point and the loss of gold, during the removal of the tellurium. The usual course is to smelt this class of ore either with lead or copper ores. It is to the latter method I will call especial attention in this paper.

In order to work the copper ores of the west economically, they are smelted with gold and silver-bearing ores which act as flux, and also enrich the matte produced to a point where the cost of refining the copper is more than covered by the value of the precious metals contained. In this way large amounts of tellurium enter the matte. These mattes are Bessemerized in the west, and copper brought east to be refined by electrolysis. It contains from 98.5 to 99.5 per cent. copper, about 100 ounces of silver, and three-tenths ounce of gold per ton. The impurities are arsenic, antimony, lead, bismuth, tellurium and selenium. The average amount of tellurium is not far from 0.04 per cent. or 0.8 of a pound per ton. With the possible exception of the native copper of Lake Superior, it is doubtful if any copper produced is free from tellurium; this is certainly true of that from sulphide ores. I have already described a method for estimating the tellurium under these circumstances.[1]

The electric refining of such copper is carried on at Anaconda and at the Boston and Montana Copper Co. works at Great Falls, Montana; the Baltimore Electric Refining Co., Baltimore, Maryland; the Bridgeport Copper Co., Bridgeport, Conn., and the Ansonia Refining Co., Ansonia, Connecticut; the Central Falls Electric Refining Co., Central Falls, Rhode Island; the Washburn and Moen Co., Worcester, Mass. and perhaps others.

In the Hayden process a bath of dilute copper sulphate, acidified with sulphuric acid is employed, in which is inserted an anode of rolled black copper and a cathode from a strip of pure copper, each being connected with the electric generator, while

[1] *J. Am. Chem. Soc.*, **17**, 280, *1895*.

disconnected plates of black copper are suspended in the bath between the two electrodes. When the current is on, solution takes place, not only at the anode but on all the disconnected plates interposed between the electrodes, and what is more interesting, this solution takes place on those surfaces of these plates which face the negative electrode, while the deposition of the pure copper takes place on the surface of the adjacent plate which faces the positive electrode. When the copper goes into the solution in its bath small amounts of some of the impurities in the copper enter into solution with it, but the greater portion remains either in the metallic state or are converted into oxides or basic salts which fall to the bottom of the bath where they form a black slimy residue.

The commercial refining of these residues is carried out as follows:

After screening out the coarser copper, the slimes are boiled with a twenty per cent. solution of sulphuric acid in a lead-lined tank by live steam, air being drawn in with the steam by means of a peculiar injector. During this boiling, practically all of the antimony, arsenic and bismuth salts, together with copper in the oxidized condition and that small portion of metallic copper which has been oxidized by the injected air go into solution.

After about one hour's boiling, a solution of silver sulphate is run in and steam applied for some minutes whereby according to the reaction $Cu + Ag_2SO_4 = CuSO_4 + Ag_2$, the metallic copper still remaining is rapidly and completely converted into copper sulphate. Any excess of silver sulphate is removed by the addition of a fresh portion of slimes, when the solution is drawn off and the residue washed until free from copper salts. This residue, which has now lost the slimy, adhesive properties which characterized it and which consists of gold, silver, tellurium, and lead sulphate is pressed on a filter press. The pressed cakes are dried in an oven and then melted in a furnace, having a bed made of Portland cement, which is so arranged that a blast may be turned on. This quickly removes all but a trace of the lead present, together with portions of the tellurium and selenium.

The resulting bullion is poured into shoe-bars, weighing about 300 ounces each, it is about 950 fine, in silver and ten parts of

gold. When cool these bars are dissolved in hot sulphuric acid, in a cast iron kettle, and when solution is complete the liquid is allowed to cool and settle for several hours, during which the gold falls to the bottom and the tellurium crystallizes out in white lustrous crystals of tellurous oxide. The first portion of the clear liquid is drawn off and precipitated by metallic copper, and the silver melted into bars 990 fine. The remainder is used in treating a fresh portion of the slimes.

The gold and the tellurous oxide are allowed to accumulate in the kettle until several hundred ounces are at hand, when they are removed and washed with dilute sulphuric acid and water, to remove silver, copper sulphate and tellurous oxide, and afterwards boiled in a small kettle with concentrated sulphuric acid to remove the remaining portion of silver and tellurium. When cool, and the gold has settled, the acid is again drawn off and the residue washed until free from tellurium and silver sulphates. The gold is now melted with borax and niter, by which any remaining traces of lead and tellurium are oxidized and slagged off, leaving fine gold, over 990 fine, the impurity being silver.

The washings from the gold residue contain the tellurium as tellurous oxide or tellurous sulphate. The tellurium may be obtained from these in two ways, after the removal of the silver as chloride. First, by precipitation with copper; second, by passing sulphur dioxide through the solution. It is better to use the first method, as large quantities of sulphur dioxide are very disagreeable to handle, and as the tellurium thus precipitated in the presence of copper is not pure and requires a further treatment. The metal used in this work was produced by inserting bars of copper into the solution and boiling with steam, a precipitate of cuprous telluride being obtained as a black powder. This was dried and then boiled with a five per cent. solution of sulphuric acid to remove the copper which had been oxidized during the drying process. After filtering, the mass is again moistened with five per cent. sulphuric acid and subjected to atmospheric oxidation with frequent stirring, then boiled again with more sulphuric acid and washed, this process is repeated until the copper is eventually very completely removed. Any copper left will combine with tellurium when fused and

cause loss. The residue is now dried, mixed with three times its weight of sodium carbonate, and one-fourth its weight of charcoal, melted in a French clay crucible to quiet fusion, brought almost to a white heat, and the melt poured into a suitable mold. The cooled mass is crushed to a powder and the sodium telluride formed, dissolved out with boiled water; a great amount of heat is developed during the solution. The solution thus produced, which psssesses a rich port wine color, is filtered off, and the tellurium precipitated in the metallic state, by the passage of a current of air, as a fine gray powder, looking not unlike finely powdered galena. The tellurium is filtered and boiled with dilute hydrochloric acid, to remove traces of iron, alumina, etc., washed and boiled for several hours, with a concentrated solution of potassium cyanide which removes selenium and most of the gold present. After drying, the tellurium is melted, without flux, in a French clay pot, the fine particles are made to run together by stirring, only a low temperature is necessary and the loss by volatilization is small. The metal still contains traces of impurities, the chief of which is gold. This would indicate that sodium telluride is a solvent of metallic gold, but this has not yet been proven. The tellurium is further purified by distillation in hydrogen gas.

NEW REACTIONS OF THE SALTS OF TELLURIUM.

If to a solution of the sodium or potasium tellurite is added a solution of an ammonium salt, such as the chloride or nitrate, a white precipitate is thrown down, which on boiling becomes granular.

$$Na_2TeO_3 + 2NH_4Cl = 2NaCl + TeO_2 + 2NH_3 + H_2O.$$

A small amount of tellurium dioxide or a metal which can be precipitated by sulphur dioxide remains in solution. It is the intention of the writer as soon as possible to examine and compare the properties of the metal from this fractional precipitation. While it is probable that tellurium oxide is slightly soluble in the alkali salts formed, which would explain incomplete precipitation, in view of the growing belief in the compound nature of tellurium, this reaction is deemed worthy of further investigation.

In an effort to purify tellurium, based upon the well-known property of hydrogen telluride of precipitating many of the

metals from solution, the following reaction was observed, in addition to the one expected: $TeCl_4 + 2H_2Te = 3Te + 4HCl$. By passing this gas for some time into a solution of tellurium chloride, made slightly acid with hydrochloric acid, there was obtained a precipitate of tellurium and tellurides and a solution, from which sulphur dioxide threw down a precipitate of tellurium. After distillation in hydrogen I propose to determine the atomic weight of this purified metal.

When potassium ferrocyanide is added to tellurium chloride no change is observed at first but after a few hours Prussian blue is formed in large quantities.

ALUMINUM TELLURIDE.

Tellurium when heated with aluminum combines with explosive violence, forming a chocolate colored, difficultly fusible compound having the following composition by analysis.

	Per cent.
Aluminum	12.78
Tellurium	87.22
	100.00

This corresponds closely to the formula Al_2Te_3 which requires

	Per cent.
Aluminum	12.58
Tellurium	87.42
	100.00

The violent chemical action attending its formation, joined with the fact that its composition remains constant, even in the presence of a large excess of aluminum, would indicate a true chemical combination and not an alloy, in the accepted sense. It is hard and brittle, can be easily ground to powder. When exposed to moist air it is slowly decomposed with the liberation of hydrogen telluride. When thrown into water hydrogen telluride is rapidly given off according to the following reaction: $Al_2Te_3 + 3H_2O = Al_2O_3 + 3H_2Te$ which corresponds to the well known sulphur reaction $Al_2S_3 + 3H_2O = Al_2O_3 + 3H_2S$. While comparing these two reactions it may be noted that hydrogen telluride is much more easily decomposed by oxygen than hydrogen sulphide. For example in treating aluminum telluride with

water which has not been boiled fully one-half of the tellurium remains as metal: $H_2Te + O = H_2O + Te$. When treated with ninety-five per cent. alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts as it does not decompose in the air so quickly as the alkali tellurides.

SEPARATION FROM COPPER BY THE ELECTRIC CURRENT.

Tellurium is easily deposited by the current, either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium fron copper by adding an excess of sodium hydroxide and about three grams of potassium cyanide for each gram of copper present. With this solution, a current such as is used for depositing copper, will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours, the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough, none of it will adhere to the cathode.

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THE ELECTROLYTIC REDUCTION OF PARANITRO COMPOUNDS IN SULPHURIC ACID SOLUTION.[1]

BY ARTHUR A. NOYES AND JOHN T. DORRANCE.

Received September 9, 1895.

INTRODUCTION.

IT was shown some time ago by Noyes and Clement[2] that nitrobenzene in sulphuric acid solution is transformed by electrolytic hydrogen into paraamidophenolsulphonic acid. It has since been proved by the extended investigations of Gattermann and his students[3] that this behavior is characteristic of aromatic nitro compounds in general, one of the oxygen atoms

[1] Read at the Springfield meeting.

[2] *Ber. d. chem. Ges.*, **26**, 990.

[3] *Ibid*, **26**, 1844, 2810; **27**, 1927.

of the nitro group always migrating during the reduction to the para position with the production of a hydroxyl group. It is evident, however, that this cannot take place when the position para to the nitro group is occupied by another element or group than hydrogen. The purpose of our investigation was to determine the nature of the reduction-products of a number of such compounds with the view of ascertaining any general principle that may exist. Only three such para compounds have been previously studied, namely, paranitrotoluene and paranitroorthotoluidine by Gattermann[1] and paranitrobenzoic acid by Noyes and Clement.[2] We have now investigated three additional ones, paranitraniline, paranitrophenol, and parachlornitrobenzene.

THE METHOD OF REDUCTION.

The method of carrying out the reduction was essentially the same in all cases. The apparatus consisted of a small beaker, to the sides of which a large platinum electrode was closely fitted, and in which was placed a cylindrical porous cup containing a small platinum electrode. Concentrated sulphuric acid was placed within the cup at the start, and small quantities of diluted acid were occasionally added during the electrolysis to prevent the acid from becoming fuming. The solution to be electrolyzed was placed outside; it was prepared by dissolving twenty or thirty grams of the substance in two and a half to three times its weight of strong sulphuric acid. A current of one or two amperes was passed through for forty or fifty hours.

The reduction-product precipitated either during the electrolysis or after cooling. It was filtered out upon a hardened filter with the aid of suction and dried by spreading on porous plates. The filtrate was diluted with an equal bulk of water, and any further precipitate added to the original one. The subsequent purification varied in the different cases, and will be described under the separate substances.

REDUCTION OF PARANITRANILINE.

The paranitraniline used was in part a Kahlbaum preparation and was in part prepared by ourselves by the method given by

[1] *Ibid.* **26**, 1850, 1852.
[2] *Am. Chem. J.*, **16**, 511.

Nölting and Collin.[1] It gave the correct melting-point of 146°.

The reduction-product was isolated by extracting the precipitate dried on the porous plates with boiling water, boiling the solution with animal charcoal, filtering, and causing to crystallize by cooling.

It was found to consist of paradiamidobenzene sulphate. It was very difficultly soluble in cold water.[2] Its solution was colored purple by ferric chloride, and it gave the following results on analysis:

0.2193, 0.2847, and 0.3581 gram substance gave respectively 0.0985, 0.1262, and 0.1638 gram water and 0.2822, 0.3672, and 0.4605 gram carbon dioxide.

0.3147, 0.2077, 0.3938, and 0.4525 gram substance gave respectively 0.3481, 0.2340, 0.4363, and 0.5066 gram barium sulphate.

	Found.				Calculated for
	I.	II.	III.	IV.	$C_6H_{10}N_2SO_4$.
Carbon	35.10	35.18	35.08	....	34.94
Hydrogen	4.99	4.92	5.08	....	4.85
Sulphur trioxide	38.32	38.68	38.04	38.44	38.84

REDUCTION OF PARANITROPHENOL.

A sample of the substance from Kahlbaum having the correct melting-point (113°) was employed.

The reduction-product was practically insoluble even in boiling water, but dissolved readily in sodium hydroxide or carbonate. It was purified by dissolving in the latter, filtering, and precipitating immediately with hydrochloric acid. The precipitate was washed successively with water, alcohol, and ether, and dried at 125°. Twelve grams were obtained from thirty grams of nitrophenol.

The physical and chemical properties and the analysis of the body established its identity as paraamidophenolsulphonic acid, It reduced silver nitrate solution in the cold with the production of a purple color, and turned brown rapidly in alkaline solution owing to oxidation. It was decomposed by heating with strong

[1] *Ber. d. chem. Ges.*, 17, 262.

[2] Contradictory statements exist in the literature as to the solubility of this salt. Nietski, in *Ber. d. chem. Ges.*, 11, 1098, states that it is readily soluble. Vignon, in *Bull. Soc. Chim.*, 50, 153, that it requires 714 parts of water at 15°. The latter statement is, according to our experience, the correct one.

hydrochloric acid in a closed tube to 180°; the hydrochlorate of the base crystallized out upon cooling, and from this, by the addition of potash, the base itself was set free. Like paraamidophenol, it melted at 183°, undergoing decomposition. It also showed the characteristic color reactions of that substance with chloride of lime and ferric chloride.

The analysis of the sulphonic acid gave the following results:

0.2361 gram substance gave 0.0879 gram water and 0.3295 gram carbon dioxide.

	Found.	Calculated for $C_6H_3.NH_2.OH.SO_3H$.
Carbon	38.06	38.08
Hydrogen	4.13	3.70

REDUCTION OF PARACHLORNITROBENZENE.

A Kahlbaum preparation (melting-point 83°) was employed in this case also. The reduction-product proved to be a sulphonic acid, and was purified exactly as that obtained from the reduction of nitrophenol. It was first tested qualitatively for chlorine and found to contain none. It exhibited in fact all the characteristic properties of paraamidophenolsulphonic acid, being almost insoluble in hot water, oxidizing very rapidly in alkaline solution, and readily reducing silver nitrate solution. It was subjected to just the same treatment as the reduction-product of the nitrophenol with identical results. In addition to the confirmatory tests described under that substance, the diacetyl derivative of the base was prepared by boiling with acetic anhydride, and this was found to melt at 149°. Diacetyl-paraamidophenol melts according to Ladenburg at 150°–151° C.

The sulphonic acid gave the following results on analysis:

0.2912 gram substance gave 0.1002 gram water and 0.4059 gram carbon dioxide.

	Found.	Calculated for $C_6H_3.NH_2.OH.SO_3H$.
Carbon	38.02	38.09
Hydrogen	3.90	3.70

SUMMARY OF THE RESULTS.

The paranitro compounds, which up to the present time have been submitted to electrolytic reduction are tabulated below together with their reduction-products:

$C_6H_4<^{NO_2\ (1)}_{CH_3\ (4)}$	$C_6H_4<^{NH_2\ (1)}_{CH_2OH\ (4)}$ [1]
$C_6H_3<^{NO_2\ (1)}_{CH_3\ (4)}_{NH_2\ (5)}$	$C_6H_2<^{NH_2\ (1)}_{OH\ (2)}_{CH_3\ (4)}_{NH_2\ (5)}$
$C_6H_4<^{NO_2\ (1)}_{CO_2H\ (4)}$	$C_6H_4<^{NH_2\ (1)}_{OH\ (4)}$
$C_6H_4<^{NO_2\ (1)}_{Cl\ (4)}$	$C_6H_4<^{NH_2\ (1)}_{OH\ (4)}$
$C_6H_4<^{NO_2\ (1)}_{OH\ (4)}$	$C_6H_4<^{NH_2\ (1)}_{OH\ (4)}$
$C_6H_4<^{NO_2\ (1)}_{NH_2\ (4)}$	$C_6H_4<^{NH_2\ (1)}_{NH_2\ (4)}$

The most striking of the results are those obtained with the paranitrobenzoic acid and with the parachlornitrobenzene, the group para to the nitro group being driven out in each case. It seems not improbable that this behavior is a general characteristic of nitro compounds with negative para groups, but an investigation of others would be needed in order to establish it as a fact.

It is also worthy of note that, contrary to what might be expected, in only one of the six cases, that of the nitrotoluidine, does the oxygen atom display any tendency to migrate to any other than the para position.

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PERIODIDES OF PYRIDINE.[2]

BY A. B. PRESCOTT AND P. F. TROWBRIDGE.

Received September 20, 1895.

PYRIDINE ALKYL PERIODIDES.

1. *Pyridine Methyl Pentiodide.*—This was obtained in the manner given in detail below, very satisfactorily in preparation I, and with slight impurity in two other preparations, II and III, by different ways, through separation from other periodides.

[1] The substance isolated was a condensation-product of this with a second molecule of nitrotoluene; but this is undoubtedly the primary reduction-product.

[2] Read at the Springfield meeting of the American Association for the Advancement of Science, September 2, 1895.

Preparation I is in greenish-black long needles of very dark green luster, some of the crystals being nearly two inches in length. The melting-point is 47.5° C.[1]

Preparation II is of small quantity, in greenish-black crystals, very hard and compact, melting at 47° C.

Preparation III is in crystals exactly like I, melting at 47° C., by recrystallization in alcohol from a greenish-black crystalline powder, the latter being stable and melting at 43° C. The analysis of III was obtained only from this powder, before the final crystallization. These three preparations are, alike, so far stable that after keeping eight months in glass-stoppered bottles, most of the time in the dark, the glass is but just perceptibly stained with iodine liberated from decomposition.

The analyses of the methyl pentiodide, by methods detailed further on, gave results as follows:

	Calculated for $C_5H_5N.CH_3I.I_4$.	Found. I.	II.	III.
Iodine total	87.06	86.74	....	86.69
Iodine by titration	69.65	68.87	69.83	69.55

2. *Pyridine Methyl Diiodide.* — Obtained through different ways, as stated later, in two preparations. I is in reddish-brown crystals, thick plates, compact in clusters. Some crystals are an inch long and a fourth of an inch wide. Melting-point, 91.5° C. The crystals are very stable. On eight months' standing there are no perceptible results of decomposition. II is in red interlaced fine needles of good length, the last previous crystallization having been in dark-red sheaf-form clusters of great beauty. Melting-point, 91.0° C. In stability II is equal to I.

The analyses, with duplicates as specified later, gave the following:

	Calculated for $C_5H_5N.CH_3I.I.$	Found. I.	II.
Iodine total	72.91	72.88	72.33
Iodine by titration	36.55	36.97	36.40

3. *Pyridine Methyl Triiodide.*—Obtained in three preparations, each from a separate recrystallization out of a common mother-

[1] Measurements of the crystals, and various optical determinations, as well as work by other physical methods, especially such as bear upon molecular weight and constitution, are reserved together for a continued investigation of these bodies.

liquor, that of II of the methyl diiodide. Again it is obtained in the first crystallization by another method, that for IV. I is in dark-red fine needles, quite perfect in outline and partly clustered in certain sheaves characteristic of the earlier crystallizations of this triiodide. Melting-point, 50° C. Perfectly stable.

II shows dark-red needles, the previous crystallization having been merely a loose crystalline mass. Obtained perfectly stable, with melting-point of 50° C.

III is dark-red needle clusters of a certain exact sheaf-form appearing illusively in several earlier crystallizations. But a small quantity was obtained, with a melting-point of 49°–50° C.

IV, perhaps the most perfect, is in very dark red or reddish-black plates with needles, perfectly stable, and melting at 48° C.

The results in analysis have been these :

	Calculated for $C_5H_5N.CH_3I.I_2$.	Found. I.	II.	III.	IV.
Iodine total.....	80.14	79.32	79.22	....	78.70
Iodine by titration....	53.43	53.08	51.52	52.75	53.15

4. A product was obtained of seeming distinct character, in composition and melting-point nearly approaching the pentiodide, but with the elemental figures of a tetrapentaiodide, that is, dipyridinedimethylenneaiodide. It is reserved for further work. It is in greenish-black, lustrous, long needles, well defined, of a melting-point of 44° C. The total iodine in three successive determinations was found to be, respectively, 85.83, 85.88, and 85.83 per cent.; calculation for $(C_5H_5N.CH_2I)_2I_7$ giving 85.68 per cent., and for $C_5H_5N.CH_2I.I_4$, 87.06 per cent. The iodine by titration was found to be 67.52, 67.08, 67.02, and 66.69; calculation giving for these formulas, respectively, 66.45 and 69.65 per cent.

5. *Pyridine Methyl Octaiodide.*—This product is named provisionally, one fairly satisfactory preparation of it being obtained, a second preparation having the requisite composition but (possibly from its more compact crystallization) having a higher melting-point, and a third preparation, while agreeing in melting-point with the first, falling too low in percentages of iodine. The preparation, detailed below, was instituted in the hope of obtaining the enneaiodide. I, by recrystallization from alcohol below

0° C., is greenish-black, in both plates and needles, melts at about 26° C., and is fairly stable when kept at about 15° C. or below. II is in crystals of the same color as those of I, but more slowly formed and more compact, consisting of flat needles, some of them an inch long, with melting-point of about 41° C.. III was imperfectly crystallized, rather solidified in a crystalline mass, of the color of I, and melting at 25° C. We do not include III among the determinate preparations. It gave of total iodine, 90.36 per cent., and of iodine by titration 78.41 per cent., both figures being low for the octaiodide and much too high for the heptaiodide.

	Calculated for $C_5H_5N.CH_3I.I_7$.	Found. I.	II.
Total iodine	91.51	90.79	90.99
Iodine by titration	80.07	79.82	80.13

6. *Pyridine Ethyl Triiodide.*—Obtained, as specified under the account of preparations, from liquid secondary products corresponding to those which gave the three samples of the pyridine methyl triiodide, in lustrous greenish-black needles, well defined, stable through exposure to the air, and melting at 49° C. In the analysis, two determinations by silver iodide gave for iodine 78.389 and 78.388. Three titrations with the thiosulphate gave for iodine 52.784, 52.612 and 52.616. Inasmuch as the mother liquids have been found to contain higher periodides, it is evident that these crystals are not wholly freed from mother liquid.

	Calculated for $C_5H_5N.C_2H_5I.I_2$.	Found.
Iodine total	77.85	78.39
Iodine by titration	51.90	52.67

7. Higher ethyl periodides of pyridine, in nearly black crystals melting below 10° C., were indicated from treatment of the primary oil-like product, though not yet obtained in purity, as stated under the preparation of the triiodide.

Methods of Preparation.—The methyl periodides of pyridine are best obtained, first, by adding the methyl normal iodide of pyridine to dissolved iodine. We have also obtained several pyridine methyl periodides; second, by adding pyridine to a solution of methyl iodide and iodine. We have found, however, as stated further on, that in the latter way there is formed some proportion of a pyridine periodide destitute of methyl, though

the avidity of pyridine for methyl iodide ensures a considerable proportion of methyl periodides. For pyridine ethyl periodides the second way would not promise formative results at all owing to the tardy addition of ethyl iodide to pyridine. The normal pyridine alkyl iodides used were prepared for the purpose, and had the properties specified in another paper by one of us (P), in which, also, is a statement of the constants of the pyridine used in these preparations. In adding the pyridine alkyl normal iodide to iodine, the latter was taken in the proportion to make the particular periodide desired, but other periodides would appear as subordinate products. As to just how much effect the relative quantity of iodine added exerts upon the extent of iodine combination, further investigation is now in progress.

The preparation of pyridine methyl pentiodide was done as follows: Eighteen grams of pyridine methyl iodide dissolved in a little alcohol were added to fifty grams of iodine previously dissolved in 200 cc. of alcohol, the solutions being taken at low temperature. A dark green oil-like liquid, thick and cohesive, at once separated in abundance at the bottom. The thin alcoholic liquid above was decanted off and the oil set aside at temperature several degrees below 0° C., when it shortly solidified in crystals, not melting at 25° C. These were dissolved in warm alcohol, and the solution set aside at about —5° C., when crystals of preparation I appeared. They were dried over sulphuric acid to a constant weight, for analysis and determination of the melting-point. This periodide was undoubtedly obtained in its amorphous oil-like state by O. Lange in 1885[1] while engaged in obtaining decomposition products of pyridine methyl iodide by Ladenburg's process. He reported obtaining the heavy dark-green oil, which would not solidify on standing for a day, and which he apparently did not analyse.[2] III of the methyl pentiodide was obtained by treating a part of the first crystalline form of the methyl octaiodide before described, with ether, which

[1] On Picolines, *Ber. d. Chem. Ges.* **18**, 3436.

[2] It was in following Lange that this preparation I of the methyl pentiodide was first undertaken, and the "oil" obtained. After fruitless attempts to crystallize it from various solvents, it was abandoned for six weeks, when, on one very cold day, in moving things it was set in the window next the glass, and presently it became a mass of crystals. These did not melt when returned to the warmer air of the laboratory. A new preparation was at once commenced as above.

dissolves a small portion of the crystals, leaving the remainder as this preparation III of the pentiodide. Preparation II of the methyl pentiodide was obtained from the mother liquor of the methyl octaiodide by evaporation and redissolving the crystals in alcohol.

The preparations of the pyridine methyl diiodide in I and II were from solutions quite different from each other from the beginning, but in both cases they were from later crops of crystals following the addition of free pyridine to solution of the other two materials. The final crystals of I were washed in a very little cold alcohol, and then dried over sulphuric acid for ten days. The crystals of II were obtained fine by rapid formation in alcohol surrounded by a freezing mixture.

The preparations of pyridine methyl triiodide in I, II and III were crystallized from the mother liquids of II of the corresponding diiodide. II of the triiodide was itself recrystallized several times. I and III were in more compact crystals of slower formation. But IV was the result of a different method throughout, following the addition of iodine solution to the methyl normal iodide, using proportions intended for the diiodide. The final crystals were by a single recrystallization of the first crop. It was dried between filter papers over sulphuric acid.

The preparations of pyridine methyl octaiodide (provisionally so termed) were instituted by adding eleven grams of the normal iodide dissolved in a little alcohol, to fifty-five grams of iodine in as little alcohol as possible, both solutions being hot. The greenish black oil-like mass separated at once. The decanted solution was cooled, and other portions of the oil obtained. Below 0° C. the oil crystallized well. I was crystallized from solution in alcohol at low temperature. II was crystallized from alcohol by spontaneous evaporation out of doors in cool weather. The final crystals of each were dried between filter papers, and kept in the vault at about 12° C.

Pyridine ethyl triiodide was obtained following the addition of alcoholic solution of the normal iodide to alcoholic solution of iodine. The first product, chiefly higher iodides, appeared in an oil-like precipitate, and this, after decanting the alcoholic liquid, was dissolved in hot alcohol, and the solution kept for six

hours at —4° C. without obtaining crystallization. Afterward crystals were obtained but without success in drying them. Moist with the oil they gave figures a little too low for the tetraiodide. Repeating the entire operation, but not decanting the oil, the entire mixture was exposed to low temperature as before, and the oil solidified in a mass of fine crystals better than before, but these melted below 10° C., and the attempt to obtain a pure high periodide had to be deferred. That the oil, which is stable when dried and has no odor of iodine, contains high iodine additive combination was shown by its analysis, giving figures midway between hexiodide and heptiodide. Now the alcoholic liquid decanted from the oil in the first operation, on cooling below 0° C., gave an excellent crop of crystals. These, dried for several days over sulphuric acid, at about 21° C., constitute the preparation described under the name pyridine ethyl triiodide.

PERIODIDES OF THE AMINE AND OF THE TERTIARY AMMONIUM BASE.

1. *Pyridine Tetraiodide*, $C_5H_5N.I_4$.—Adding to pyridine an alcoholic solution of iodine until the precipitate ceased to form, thereby leaving a slight excess of iodine, there was obtained a bulky crystalline precipitate of a green color, not of a red color as reported by Dafert.[1] This precipitate was filtered out, drained, washed with alcohol, and drained dry, all under the filter pump, then dried between filters over sulphuric acid for several days. It was found soluble in alcohol, ether, chloroform, and less readily in benzene. It was recrystallized from benzene in I, from chloroform in II, and from alcohol in III. In each result the crystals were dark lustrous green. Those of III were in button-like aggregations of fine needles, the whole about half an inch in diameter. From each solution the crystals showed the same melting-point, 85° C. The alcoholic mother-liquor on evaporation gave a crop of very small dark-green crystals IV of the same melting-point. All these crystals gave off perceptible traces of iodine on standing in a glass-stoppered bottle, being very perceptibly less stable than the crystal preparations of the various pyridine *quaternary* base periodides already described. This instability may be the cause of the slight deficiency of iodine found in analysis, the resulting figures being as follows:

[1] *1883*, Monatsh. Chem., 4, 509.

	Calculated for $C_5H_5N\,I_4$.	Found. I.	II.	III.	IV.
Iodine total, by silver iodide	86.49	85.72	85.94	85.63	85.48
Iodine by titration with thiosulphate		85.05	84.79	85.73	85.63

This periodide, therefore, contains no iodine firmly bound as in all normal iodides, none that is not promptly taken up by thiosulphate. In this constitutional feature it is a periodide sharply unlike all the pyridine alkyl periodides known, and unlike the pyridine hydrogen pentiodide found by Dafert,[1] and further described below as examined by us. A superbromide of pyridine was obtained, in 1882, by Grimaux,[2] who writes for it the formula, $(C_5H_5NBr_2)HBr$. He found it not very stable; in analysis he made but one estimation of bromine, that by silver bromide; and he found the compound reduced by hydrogen sulphide to pyridine hydrobromide and hydrobromic acid. The triethylphosphine tetraiodide, $P(C_2H_5)_3I_4$, *inferred* by Masson and Kirkland in 1889,[3] is of the same type as our pyridine tetraiodide. Treated with hydrogen sulphide half its iodine entered into phosphonium normal iodide, and half into hydriodic acid.

Several months before the preparation of pyridine tetraiodide as above given, a product was obtained in another way which puzzled us at the time, but which we now recognize as this last-formed pyridine tetraiodide. It was obtained in the first crystalline precipitate after adding free pyridine to the solution of methyl iodide and iodine, in the second way for making the methyl periodides. The mother-liquor of the precipitate gave us the methyl diiodide, preparation I of that product. The precipitate itself crystallized from a chloroform solution, gave very dark green short needles, melting at 84.5° C., and soluble in ether and in benzene. The total iodine was found as 86.32 per cent (the average of four results, lowest 86.22, highest 86.50). At that time a satisfactory titration for iodine was not obtained

[1] F. W. Dafert, *1883*, Monatsh. Chem., 4, 508. Dafert says, p. 509, "In alkoholischer und in wässeriger Lösung des Pyridins erzeugt Iod in Alkohol, respective in Iodjodkaliumlösung ebenfals unter gewissen umständen eine Fällung. Eben so bei Anwendung von Schwefelkohlenstoff. Das dabei erhältene Präparat ist roth gefärbt und jedenfalls mit dem obigen Superiodid *nicht* identisch. Eine weitere Untersuchung wird wohl näheres ergeben." We have not been able to find a further publication by Dafert upon this compound.

[2] E. Grimaux, *Compt. rend.*, 95, 87; Bull. Soc. Chim., 38, 127.

[3] *J. Chem. Soc.*, 55, 139.

on account of the solvent, but without any solvent one slow titration resulted in 85.82 per cent., indicating the absence of normal iodine, when the preparation was put aside for later inquiry. It appears, therefore, that when free pyridine is added to methyl iodide and iodine, in alcoholic solution of each, some periodide of pyridine without methyl is formed in the first precipitate, notwithstanding the extreme avidity with which pyridine unites directly with methyl iodide.

2. *The Pyridine Hydrogen Pentiodide of Dafert.*[1]—This was obtained, following the plan given by that author, in crystals such as described by him, melting at about 85° C. (Dafert 89° C.) In analysis it gave 88.03 per cent. of total iodine, and 70.20 per cent. of iodine by titration (calculation for $C_5H_5N.HI.I_4$, total iodine 88.77 per cent., and superiodine 71.02 per cent.). For the titration the periodide was dissolved in alcohol, the end reaction was sharp, and the result conclusive as to the fundamental difference between the two compounds, one of which we believe to be a periodide of C_5H_5NH, and the other of C_5H_5N.

A hydrogen periodide of pyridine, therefore, like alkyl ammonium periodides in general, includes for each atom of nitrogen (in the molecule whatever its magnitude) just one atom of iodine which is left united to the nitrogen after the action of reducing agents of sufficient strength. On the contrary the periodides of pyridine not having ammonium hydrogen or alkyl contain no iodine left by such reducing agents in union with the base, as we say, no iodine firmly bound. Various forms of these two types may be represented as follows:

(1) $R_4NI.I_n$, quarternary alkyl ammonium periodides.
$(R'''N)RI.I_n$, quarternary pyridine periodides.
$(R'''N)HI.I_n$, pyridine hydrogen periodide.

(2) $(R'''N).I_n$, pyridine (amine) periodide.
$(R'''N)Br_2HBr$, a superhalide (Grimaux).
$R_3PI_n.I_n$, inferred by Masson and Kirkland.

ESTIMATIONS OF THE IODINE OF PERIODIDES.

1. The total iodine is obtained by precipitation as silver iodide, weighing this on filters to be described later.

[1] *1883:* Monatsh. Chem., **4**, 508.

The sample is weighed, from a weighing bottle, by difference into a No. 2 beaker. About twenty cc. of a saturated solution of sulphurous acid is added, then a slight excess of silver nitrate solution (used of known strength). The mixture is heated on the water-bath for about an hour, breaking the crystals of periodide if necessary with a flat end of a glass rod, then acidulated strongly, using twenty to thirty cc. of nitric acid, (sp. gr. 1.20), and heated one to two hours or until the precipitate is of a uniform light straw color and the liquid perfectly clear. The precipitate is then put upon the prepared funnel of ascertained weight and washed, first with five per cent. nitric acid and then with hot water, using the pump throughout. The funnels are small sized "carbon tubes," the bottom loosely fitted with a glass plug or shoulder, on which is a layer of cracked glass, twelve to twenty mm. thick, made from beakers and sieved to pass a ten-mesh but not a twenty-mesh. After this is washed level, under pressure of the filter-pump, a layer of acid-washed asbestos is floated over it, and the whole dried at 130° to 150° C. for about two hours or for constant weight. Weighing is done with duplicate funnels, suspending them with an aluminum loop.

The washed silver iodide in the funnel is dried, with its duplicate (also wetted), for two hours at 130° to 150° C., or until weight is constant. A set of about thirty of the funnels have been in hand, and when all have been used, the asbestos layer and precipitate are carefully removed, and a fresh asbestos layer floated on, all which can be done for the set in about two hours.

Two to four parallel estimations have been made, and the average taken. The agreement of the estimations is fairly shown in these figures, quoted from the results: 86.69, 86.79, 86.84, 86.66; 72.45, 72.08, 72.45 ; 86.65, 86.29.

2. The iodine in excess of that for a normal iodide, that is, the iodine responding to reducing agents, has been estimated volumetrically by thiosulphate, using a solution of which one cc. equals 0.010 of iodine. To make this solution, "C. P. sodium thiosulphate" is recrystallized small by stirring while the solution cools. The volumetric solution is standardized by standard solution of potassium dichromate, which in turn is checked with one standardized with "chemically pure" iron wire. The dichro-

mate is purified by fusing a chemically pure article and pouring upon a tile. The factor of the thiosulphate solution is taken every two or three days. The periodide analyzed is weighed by difference, from a weighing bottle into a No. 3 beaker, taking 0.150 to 0.600 gram. Of alcohol from ten to fifteen cc. are added. All the periodides so far obtained are soluble in cold alcohol, but with much difference in the readiness and abundance of this solubility, and this property governs the speed of the estimation. The crystals can be broken under a flat end of a rod, and if not readily soluble, the titration is commenced before solution is completed, keeping down the excess of the iodine-like color. At the end starch can be used as an indicator, but after practice this is not necessary, as the extinction of the iodine-like color can be read to within one drop of the thiosulphate. The burettes had been calibrated and were used with a table of corrections. Other solvents have been tried but alcohol proves far the best for the crystals in titration. Two to four titrations have been made and the average given in each estimation. The agreement of the titrations is represented by a few quotations: of the pyridine methyl diiodide, 37.01, 37.24, 36.48, 37.17; pyridine methyl triiodide, 78.55, 78.84.

UNIVERSITY OF MICHIGAN.

ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND ARSENIC.[1]

BY LAUNCELOT ANDREWS.

Received September 9, 1895.

THE experiments described in the present paper were carried out under my direction during the last winter by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch,[2] and of Jannasch and Schmitt[3] on the same subject. All experiments referred to here, relate to the analysis of an alloy containing in round numbers eighty per cent. lead, thirteen per cent. antimony, seven per cent. tin. The exact composition of this metal will be given later.

[1] Read at the Springfield meeting.

[2] *Ber. d. chem. Ges.* **27**, 3335. [3] *Zischr. anal. Chem.*, **9**, 274.

FIRST METHOD.

The attempt was made to drive off all tin and antimony as chlorides according to Drown. To this end one gram of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to 200° C. The latter was moistened with about four cc. fuming hydrochloric acid and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilizing all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as follows: Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing ten cc. of nitric acid of 1.50 sp. gr., and then through a combustion tube of large diameter, thirty cm. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion tube is covered with an asbestos tent and heated by means of an Argand burner to 210° C. The amount of the alloy used in each experiment was a half gram, and in two hours, during which time the operation required no attention whatever, the separation was complete and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion tube with hydrochloric acid. The small amount of arsenic present was easily separated from

the contents of the receiver by distillation according to Gooch and Phelps.[1] After the removal of the arsenic, tin and antimony were separated by Carnot's method,[2] which was found to be excellent.[3]

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

ANALYTICAL RESULTS.

	I. Gram.	II. Gram.	III. Per cent.	IV. Per cent.
Alloy taken	0.5000	0.5000	....	....
Lead sulphate	0.5849	0.5853	....	....
Lead found	0.3988	0.3991	79.75	79.82
Antimony trisulphide	0.0925	0.0925	....	....
Antimony found	0.0661	0.0661	13.21	13.21
Stannic oxide	0.0434	0.0437	....	....
Tin found	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total			99.92	100.05

SECOND METHOD.

It has been observed that when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidizing action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was

[1] *Ztschr. anal. Chem.*, 7, 123.

[2] *Ztschr. anal. Chem.*, 88, 650.

[3] In this method, the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

confirmed by an experiment in which potassium iodide took the place of the bromide.

One gram of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide, (about one gram) was entirely disintegrated. The antimony remained undissolved as a dark gray powder. It was filtered from the boiling solution through a Gooch filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent. too high if the metal is weighed directly.

ANALYTICAL RESULTS.

	I.	II.	
Metal taken	1.0000	1.0000	grams.
Antimony weighed direct	0.1385	0.1375	
Antimony trisulphide	0.1827	0.1833	
Antimony calculated	0.1305	0.1310	
Antimony	13.05	13.10	Per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II gives the figures obtained by the first method above described. Column III those of the second method. Column IV the mean of all of the results.

SUMMARY.

	I. Per cent.	II. Per cent.	III. Per cent.	Mean. Per cent.
Arsenic	0.13– 0.12	0.12	0.14– 0.13	0.128
Antimony	13.13–13.15	13.21–13.21	13.05–13.10	13.14
Tin	6.83– 6.84	6.84– 6.88	.....	6.85
Lead	79.87–79.95	79.75–79.82	.....	79.85
Total				99.97

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500° which are difficult to secure with certainty by means of a Bunsen or even in some cases by the ordinary forms of air-bath. The

device consists simply of an ordinary Argand gas burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at 400°, but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, etc., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate.

THE DETERMINATION OF GRAPHITE IN PIG-IRON.[1]

BY P. W. SHIMER.

Received September 16, 1895.

THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic-carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidizing action of the solvent. But, experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydrochloric acid are due to the presence, in the graphitic residue, of titanium carbide,[2]

[1] To be read at the Atlanta meeting of the American Institute of Mining Engineers.

[2] See *Trans. Am. Inst. Min. Eng.*, **15**, 455.

and possibly of other insoluble carbides, the carbon of which is, of course, included with the graphite in the final determination. In the nitric acid method, the titanium carbide is easily dissolved, and its carbon appears with the combined carbon, when the latter is determined by difference between graphitic and total carbon.

The method by solution in dilute sulphuric acid is open to the same objection as that by solution in hydrochloric acid; for titanium carbide is insoluble in sulphuric acid, and, I may add, it is also unattacked by hydrofluoric acid, and by a boiling solution of caustic potash.

The following is an analysis of a pig-iron unusually high in titanium:

	Per cent.
Silicon	3.650
Phosphorus	1.145
Sulphur	0.010
Manganese	0.226
Graphitic carbon	3.206
Combined carbon	0.128
Titanium	0.399
Iron (by difference)	91.236
	100.000

The total carbon in this iron was determined by dissolving in an acidified solution of double chloride of copper and potassium, and subsequent combustion. The graphite was determined by solution in dilute nitric acid and combustion. A determination of graphite, made by solution in hydrochloric acid and combustion, gave 3.327 per cent. of graphite, a result 0.121 per cent. higher than that obtained by the nitric acid method. The amount of carbon combined as titanium carbide (TiC) with 0.399 per cent. of titanium is 0.1 per cent., which counts as graphite in the determination by solution in hydrochloric acid. The results may be set down as follows:

	Per cent.
Total carbon	3.334
Graphite by nitric acid solution	3.206
Graphite by hydrochloric acid solution	3.327

The error in the hydrochloric acid method falls heavily upon

the resultant estimate of combined carbon, which is determined by difference, as appears below :

	Per cent
Combined carbon, when graphite is determined by nitric acid	0.128
" " " " hydrochloric "	0.007

An experiment was made to determine the action of boiling nitric acid (1.20 sp. gr.) on the graphite from this iron. A sample of two grams was dissolved in hydrochloric acid (1.10 sp. gr). After washing the graphitic residue with water, it was boiled gently for one hour with nitric acid (1.20 sp. gr.), with the addition of a little water from time to time, to keep up the bulk of the solution. The graphite as thus determined, was 3.203 per cent. against 3.206 per cent., by direct solution in nitric acid, showing that the treatment, for one hour, with boiling nitric acid, had dissolved out the titanium carbide without having attacked the graphite. The graphite in this high silicon iron, however, was coarse and perhaps unusually resistent to the oxidizing action of nitric acid. It is proposed to make similar experiments on the graphite from a variety of pig-irons.

The 0.128 per cent. of combined carbon is made up as follows :

	Per cent.
Carbon combined with 0.399 per cent. titanium as TiC	0.100
Combined carbon soluble in hydrochloric acid (probably combined with iron and manganese)	0.007
Carbon possibly existing as insoluble carbide other than titanium carbide	0.021

A careful mechanical separation of a few grams of titanium carbide was made from several pounds of this iron by use of the long, slightly inclined glass plane described in the paper before the Institute referred to above.

Besides titanium and carbon in this separation, there is some vanadium, apparently also existing as an insoluble carbide, which would account for a part of the above 0.021 per cent. of combined carbon. This investigation is, however, still under way.

The writer has never encountered a pig-iron free from tita-

nium, the amount found varying usually from 0.05 to 0.40 per cent. In irons with a coarsely crystalline fracture, the cubical crystals of titanium carbide may always be found when carefully looked for. The conclusion seems to be fair that the hydrochloric acid method includes, with the graphite determined by it, the carbon existing as insoluble titanium carbide. With pig-irons containing from 0.05 to 0.40 per cent. of titanium, the graphite so determined will be from 0.013 to 0.100 per cent. too high, while the combined carbon will be correspondingly low.

It follows that more light would be thrown upon the condition of the carbon in pig-iron by making three determinations: *viz.*, one of total carbon, one of the carbon insoluble in hydrochloric acid, and one of graphite by the nitric acid method. We would thus have determinations of graphitic carbon; carbon combined with iron and manganese, soluble in hydrochloric acid; and carbon combined as carbides insoluble in hydrochloric acid. In high-silicon, low-sulphur titanic irons, the insoluble form of combined carbon exceeds the carbon existing as soluble carbides of iron and manganese. It is important to know how the carbon is combined. One-tenth per cent. of carbon combined with titanium in the condition of disseminated microscopic crystals, probably has no effect on the hardness of pig-iron; while the same amount of carbon, combined with iron and manganese, would have an appreciable hardening effect. Practically, therefore, it may be desirable to have the carbon existing as carbides insoluble in hydrochloric acid appear with the graphite as determined by the hydrochloric acid method, although the actual graphite can be determined only by solution in nitric acid. At all events it is essential to know by what method graphite has been determined, in order to draw conclusions from determinations of graphitic and combined carbon in pig-iron.

LAFAYETTE COLLEGE, EASTON, PA.

ON THE COMPOSITION OF PELAGINE.

By A. B. Griffith and Charles Platt.

Received October 7, 1895.

THE chemical composition and constitution of the violet pigment of Pelagia (one of the Medusae) has been established by us, as follows: By treatment with hot alcohol and ether the pigment and fats are dissolved and the solution, after filtration, is evaporated carefully to dryness. The residue is treated with a solution of sodium hydroxide and the pigment then rapidly extracted by means of carbon disulphide. Upon the spontaneous evaporation of the solvent, the violet pigment is obtained as an amorphous residue.

Analysis of this pigment gave the following results:

I.	Substance employed	0.2058	gram.
	Carbon dioxide	0.47325	"
	Water	0.0810	"
II.	Substance employed	0.4605	"
	Nitrogen	15.15	cc.
	Barometric reading	742.	mm.
	Temperature	15°	

Reduced to percentages and calculating the formula the following results are obtained:

	I.	II.	Calculated for $C_{20}H_{17}NO_7$.
Carbon	62.71	....	62.66
Hydrogen	4.38	....	4.43
Nitrogen	....	3.75	3.66
Oxygen	....	....	29.24

Analysis, then, would indicate the formula $C_{20}H_{17}NO_7$. Pelagine is soluble in alcohol, in ether, and in acetic acid; it is insoluble in water, but it is very soluble in carbon disulphide. Solutions of the pigment are decolorized by exposure to light and, on spectroscopic examination, do not yield characteristic absorption bands. It has, apparently, no respiratory function and probably belongs to the same order of pigments as tetronerythrin,[1] rhodopsin, etc.; in other words, pelagine is probably a lipochrome or a nitrogenous derivative of that class. In certain respects it may be said to resemble melaine, the pigment of Sepia, investigated by Girod, Variot, and Desfosses.[2]

1 *Compt. rend.*, 93, 1029.

2 *Compt. rend.*, 93, 97.

ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

By H. L. Wells and W. L. Mitchell.

Received July 22, 1895.

THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago, F. Pisani[1] stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet color no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyze a large number of titanic iron ores and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of

[1] *Compt. rend.*, 59, 289.

the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidized under such circumstances.

Marignac,[1] with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time, but the feature of his process which is interesting in the present connection is that he reduced the titanic acid by means of a long rod of pure zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac by using sulphuric acid solutions and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:

Five grams of very finely pulverized ore are placed in a rather large beaker covered with a watch-glass and treated with about 100 cc. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and when no further action is apparent about fifty cc. of a mixture of equal volumes of concentrated sulphuric acid and water are added and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 cc. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a liter flask. With many titanic ores this operation will have dissolved everything except silicious matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium

[1] *Ztschr. anal. Chem.*, 7, 112.

disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the liter flask. Filtration may be omitted here, or in the case of the original solution, provided that the silicious matter is not to be weighed.

The liquid in the liter flask is diluted to the mark and mixed, and four portions of 200 cc. each, representing one gram of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 cc. capacity, and the other two into ordinary flasks of 350 cc. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about twenty-five cc. of concentrated sulphuric acid are added, then in each case three or four rods of chemically pure zinc, about fifty mm. long and six or seven mm. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them

near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty minutes, then, without interrupting the boiling, a glass tube, so bent that it extends fifty mm. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid (TiO_2).

When a fifty cc. burette is used, the most convenient strength for the permanganate solution is when one cc. is equal to about 0.014 grams of metallic iron, corresponding to seven and nine-tenths grams of potassium permanganate per liter.

It is customary in this laboratory to standardize permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated because they have an equal effect upon the standardization and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 cc. flask is half filled with sulphuric acid, (the strong acid diluted with about eight volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and after the air has been expelled, about six-tenths gram of the purest iron wire, representing nearly the average amount of iron in one gram of an ore, is dropped in and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidizing agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride, K_2TiF_6, was recrystallized twice from water and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid and the amount of zinc used. The following table gives the results obtained in grams:

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	—0.0090
0.6425	0.1225	0.1285	—0.0060
0.7778	0.1524	0.1555	—0.0031
0.6793	0.1308	0.1358	—0.0050
0.8226	0.1607	0.1645	—0.0038
1.0956	0.2107	0.2191	—0.0084
0.4451	0.0848	0.0890	—0.0042
0.6359	0.1215	0.1271	—0.0056
0.9004	0.1715	0.1800	—0.0085
0.4634	0.0882	0.0926	—0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by recrystallizing it, and it is exceedingly difficult to obtain any titanium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method

would be increased by adding one-twentieth or one-thirtieth to the amount of titanic acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken	Titanium Found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter.

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ARSENIC IN GLYCEROL.[1]

BY G. E. BARTON.

Received September 9, 1895.

IN following up the literature of glycerol I find that the first to note the presence of arsenic in the medicinal article was Jahns,[2] but he apparently did not investigate the subject thoroughly.

E. Ritsert[3] was the next to take the subject up. He showed the presence of arsenic in seven samples of medicinal glycerol, by the following test, which he says shows 0.001 mg. in one cc. while the Marsh test shows only 0.01 mg. in one cc. One cc. of glycerol is placed in a small measuring cylinder and to this one cc. of water is added, together with fifteen drops of hydrochloric acid and 0.6 gram zinc. The top of the cylinder is covered with filter-paper, moistened with a 1 : 1 silver nitrate solution or saturated mercuric chloride solution, and a yellow stain is obtained on the paper if arsenic is present. Ritsert also states that ammoniacal silver nitrate solution is a good reagent for arsenious acid and that the arsenious acid present probably

[1] Read at the Springfield Meeting.

[2] Pharm. Ztg., *1888*, 652.

[3] Pharm. Ztg., *1888*, 715, and *1889*, 104, 360 and 625.

explains the difference in the indications given by litmus and phenolphthalein as observed by him. He gives as the probable source of the arsenic found, the sulphuric acid used in the course of manufacture. Issue is taken with G. B. Smith,[1] who states that glycerol itself reduces silver nitrate, and hence ammonio-silver nitrate can not be used to detect arsenic.

An abstract of an article by G. Vulpius[2] gives the cost of an article free from arsenic as ten per cent. more than the current price.

L. Siebold[3] on "Arsenic in Glycerol," finds from one in 4000 to one in 6000 parts of arsenious acid in glycerol used for perfuming and medicinal purposes, and in one case one part in 2500 parts. All glycerols free from arsenic were traced to one process described as that "by which as a rule glycerol used for dispensing purposes is understood to be made." He ascribes the presence of arsenic in some cases to the solution of the arsenic present in the glass of the bottle, but this has never been confirmed and hardly seems probable.

Dr. Benno Jaffé[4] attacks the ammonio silver nitrate test which he claims to be of no value as it does not give constant results, either for arsenic or acrolein and similar bodies.

J. Luttké,[5] after an elaborate examination of twenty-one samples confirms Jaffé's conclusions and points out as among the disturbing causes, chlorides and organic acids.

There can be no doubt of the presence of arsenic in some glycerol, but I have found no one except Siebold who has attempted to give any idea of the quantity, and while he does not give the method used in obtaining the results stated, I infer from the text that, using either silver nitrate or mercuric chloride to absorb the hydrogen arsenide, he has compared the depth of color obtained with that given by known quantities of arsenious acid. A few experiments led me to think that this cannot be a very accurate method at best, so I set about to apply the method given by Sanger, for the estimation of arsenic in wall paper,[6] which

[1] Ned. Tijscnr. v. Pharm., *1889*, 143.
[2] Apoth. Zeit., *1889*, **4**, 439; *J. Soc. Chem. Ind.*, **8**, 639.
[3] Pharm. J. Trans. [3], **20**, 205.
[4] Chem. Ztg., *1890*, **14**, 1493.
[5] Apoth. Ztg., *1891*, **6**, 263.
[6] Proc. Amer. Acad., **26**, 24.

consists of comparing the mirrors obtained in a modified form of the Marsh apparatus with those prepared from known quantities of arsenious oxide in solution as sodium arsenite.

The apparatus as described by Sanger consists of a constant hydrogen generator, filled with chemically pure sulphuric acid and zinc, a smaller reduction flask having a thistle tube for introducing acid and solutions to be treated and which of course contains a small amount of chemically pure acid and zinc, a drying tube containing calcium chloride, and finally a reduction tube in which the mirror is obtained.

The cost of using chemically pure acid and zinc in the constant hydrogen generator would of course be great, and the first point I turned my attention to was a method for purifying the hydrogen generated by impure acid and zinc so that the constant generator could be run at a reasonable cost. I found that by passing the hydrogen through silver nitrate solution, the arsenic was removed entirely, according to the well-known reaction:

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 3Ag_2.$$

Another improvement in the apparatus as I used it was the substitution of a small separating funnel for the thistle tube in the reduction flask. This prevented the escape of any gas at that point while the former arrangement allowed a variable quantity to escape.

The apparatus as finally used in this work, consisted of a constant hydrogen generator, using impure acid and zinc, a wash bottle containing silver nitrate solution, a wash bottle containing water to remove any traces of silver nitrate solution which the gas might carry mechanically and which would otherwise hold back some of the arsenic in the reduction flask, a reduction flask, with separating funnel as before described, a drying tube containing calcium chloride, and finally the reduction tube.

The efficiency of the silver nitrate solution was proven by running over one hundred hours without obtaining a mirror, whereas a mirror could be obtained in from five to ten minutes from the same hydrogen not passed through silver nitrate. Using the ordinary acid and zinc of the laboratory, I found an amount of silver nitrate solution representing one gram of the salt prevented the formation of a mirror for over two hundred hours.

The mode of operating did not differ essentially from that described by Sanger. The apparatus was first filled with hydrogen, the reduction flask containing at this time only the pure zinc, of which about three grams were used. The jet at the end of the reduction tube was then lit and the tube heated at the proper place, after which a little sulphuric acid was introduced into the reduction flask and the action allowed to go on for a few minutes to prove the purity of the reagents. The solution to be treated was then added and washed in by more acid, or water where the glycerol was added directly to the flask.

The acid used was about one to eight and by slightly varying these proportions it was found possible to get along without cooling the flask. No two samples of zinc were found to contain the same amount of carbon or at least to dissolve with the same rapidity so that a careful adjustment of the acid is necessary for each lot and as large an amount as possible should be granulated at one time. It is also necessary to have standard mirrors made at different speeds to counterbalance the slight differences which are unavoidable.

The calcium chloride tube should be carefully looked after in order that the gas may be perfectly dry. I have found it best to ignite the article furnished by the makers before using. It is also a good plan to attach the bellows and blow through it a few moments after filling, to remove any slight amount of dust that might otherwise be carried into the reduction tube.

The glass used for the reduction tube should be of the hardest obtainable. I have found great variations in different pieces of the same lot. It would be of advantage if glass were carefully selected, and if necessary carefully tested, could be quoted by dealers, as otherwise a large amount of tubing is accumulated too hard for ordinary work but not hard enough for this purpose. Great care should always be taken to get tubes uniform at the point of deposition and in spite of this it was found necessary to have several mirrors of each grade.

A small white mirror was found to form beyond the arsenic mirror in those tubes representing small amounts but in those obtained from larger amounts either wholly or partly coinciding. In the latter case the arsenic mirror took on a totally different

color, the characteristic brown of the pure arsenic mirror becoming black. This mirror was without doubt in some cases partly due to moisture, and showed minute drops when examined under a lens. It also seemed to be less with the harder glasses. After having used fresh calcium chloride and the hardest glass obtainable, the only resource is in having standard mirrors representing all possible variations.

Another trouble was found to be the deposition of the arsenic in two mirrors entirely apart. This Gooch and Moseley[1] suggest to be due to the formation of two allotropic forms of arsenic by the too high heating of the reduction tube. They avoid this by enclosing the reduction tube in an iron or nickel jacket. Here again several mirrors of each standard amount are a remedy.

Having obtained a sufficient number of standard mirrors eight samples of glycerol, such as is ordinarily sold by the druggists of this city were procured. Six represented the best American makers and two were imported.

Five grams of each sample were treated with five cc. of a mixture of thirty parts sulphuric acid and one part nitric acid and the mixture heated carefully with constant stirring till a dry charred mass giving off sulphur dioxide was obtained. This was then allowed to cool and about ten cc. of water added and then the mass again heated till sulphur dioxide was given off. After cooling about fifteen cc. of water was added and the mixture boiled vigorously to expel sulphur dioxide. The liquid was then filtered off and water added as before, boiled and again filtered. This was repeated twice to insure the complete extraction of the arsenic from the charred mass. The solution thus obtained was added to the reduction flask and the usual process carried out. Five of the eight samples showed arsenic in variable amounts.

To prove that arsenic, if present, would be shown by this course of manipulation, five grams of glycerol showing no arsenic were weighed out and one cc. of an arsenic solution added. This mixture was treated exactly as the other samples had been and no arsenic mirror obtained. From this and the comparison

[1] Am. J. Sci., 48, 294.

of these mirrors with those obtained by other processes, I concluded that some, at least of the samples contain, or are decomposed into something capable of holding black arsenic. This leads to the query: What is the effect of the combined glycerol present in the toxicological examination for arsenic? May not the trouble with the glycerol be due to a decomposition product which would also be formed in the supposed case? I have not had time to investigate this important point.

Five grams of the same glycerol used in the previous experiment were then added direct to the reduction flask after diluting with water and arsenic in small quantities was obtained. One cc. of the arsenic solution was then added to the glycerol and, after diluting, the reduction carried out at once as in the previous experiment and an amount of arsenic equal to that in the one cc. of solution and five grams of glycerol, obtained. After trying several plans this method was finally chosen as both the quickest and most accurate.

The following quantities of arsenious oxide (As_2O_3) were obtained in the eight samples:

No.		No.	
1	trace.	5	faint trace.
2	0.08 mg.	6	trace.
3	faint trace.	7	0.004 mg.
4	none.	8	0.003 mg.

To prove that the mirrors obtained were due to arsenic and nothing else, mirrors were heated gently and moist hydrogen sulphide passed through them. In this manner part of the arsenic was changed to the yellow sulphide. Some of the gas from the reduction flask was passed into silver nitrate solution and a black precipitate of metallic silver obtained. On carefully neutralizing with ammonium hydroxide a yellow precipitate of silver arsenite, soluble in excess, and also in nitric acid was obtained. The nitric acid solution was precipitated with hydrochloric acid, a clean copper wire added and the solution warmed. A grey coating formed on the copper. Blank experiments showed the reagents to be pure.

From the above there can be no doubt but that arsenic was present in the glycerols examined.

The method mentioned by several authors, namely, diluting

the glycerol with an equal volume of water, adding hydrochloric acid and then metallic zinc, and obtaining a yellow coloration on a filter-paper moistened with either silver nitrate solution (1 : 1) or saturated mercuric chloride solution was tried. A twenty-five cc. measuring cylinder was used and the paper fastened tightly over the mouth, the gas escaping at the nose. In this manner using the silver nitrate solution the test was found to be about five times as delicate as the Marsh test used, and a trace of arsenic was found in sample No. 4, which had shown none in the Marsh test. The coloration was not permanent enough, owing to the action of light and other causes to be compared with standards made with permanent coloring-matters. The test with mercuric chloride, carried out in the same way, was not quite as delicate as the Marsh test. It would hardly be possible by comparing with standards to make this a quantitative method as accurate as the Sanger-Berzelius-Marsh test. It is to be noted that sample No. 2, which showed the largest amount, contained 0.08 arsenious oxide or one part in 62500, while Siebold reports as much as one part in 2500 in one case. Seventy mg. is the smallest dose known to have produced death according to Tanner[1] which would be equivalent to the amount in over four liters of glycerol No. 2, or to 150 cc. of Siebold's worst sample. Although arsenic is slowly eliminated from the system, still it would be quite possible by the indiscriminate use of sample No. 2, for some time, to accumulate enough in the system to cause death. Certainly the above figures are worthy of note by persons using glycerol for medicinal purposes.

So-called C. P. glycerol is often recovered from the waste products of the soap manufactories, and in this case the presence of arsenic is accounted for as follows: Starting with arsenical oil of vitriol, the arsenic is changed in the hydrochloric acid still to the chloride, which distils over with the acid. On neutralizing the spent lyes with hydrochloric acid the arsenic remains in the solution and is repeatedly distilled over with the glycerol.

In this connection I may say that I found no hydrochloric acid in this laboratory free from arsenic as shown by the yellow stain in the silver nitrate test, but had no trouble in preparing such

[1] Memoranda of Poisons, p. 69.

an article from chemically pure sulphuric acid which I had proven to contain no arsenic.

In conclusion I take pleasure in acknowledging my deep indebtedness to Dr. Charles E. Munroe for his many suggestions.

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THE OCCURRENCE OF TRIMETHYLENE GLYCOL AS A BY-PRODUCT IN THE GLYCEROL MANUFACTURE.[1]

BY ARTHUR A. NOYES AND WILLARD H. WATKINS.

Received September 9, 1895.

DURING the past winter our attention was called to an unusual difficulty experienced by one of the soap-making firms in the neighborhood of Boston in obtaining their glycerol of the required commercial gravity. The information furnished in regard to it indicated the presence in the glycerol of some uncommon impurity, and a considerable quantity of the "light stuff" having been generously placed at our disposal by the soap company, we were enabled to investigate it. It was submitted to fractional distillation, first at diminished and then at ordinary pressure, and a liquid boiling between 214° and 217° at 760 mm. pressure was thus separated from it. This liquid was found to have a specific gravity of 1.056 at $\frac{20°}{15°}$, and gave the following results on analysis:

0.2293 gram substance gave 0.3998 gram carbon dioxide and 0.2158 gram water.

	Found.	Calculated for $C_3H_8O_2$.
Carbon	47.52	47.37
Hydrogen	10.46	10.53

The substance is therefore trimethylene glycol, which has a boiling-point of 214° and a specific gravity at $\frac{18°}{0°}$ of 1.0526. The isomeric propylene glycol boils at 188°–189° and has a specific gravity of 1.0403 at $\frac{19.4°}{0°}$. The "light stuff" contained a very considerable proportion, about thirty-eight per cent. of glycol.

The origin of the glycol is a matter of considerable interest. There is little doubt that it was produced by fermentation of the

[1] Read at the Springfield meeting.

glycerol. For it has already been shown by Freund[1] that trimethylene glycol is, in fact, one of the principal fermentation products of that substance. It is moreover highly probable that the glycol was present in the fat before saponification by the alkali, as the fermentation can hardly have taken place in the soap lye, both on account of its saline character, and on account of the short time intervening between the saponification and the recovery of the glycerol. It had probably been produced in the fat by spontaneous saponification and subsequent fermentation of the glycerol.[2] Refuse house fat formed a considerable part of the soap stock.

The presence of the glycol in glycerol used for making nitroglycerol might be a source of danger, since it reacts with nitric acid with explosive violence. Its presence would be detected in the usual examination by a low specific gravity accompanied by a high oxidation equivalent as shown by the bichromate titration.

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THE EVOLUTION METHOD FOR THE DETERMINATION OF SULPHUR IN WHITE CAST-IRON.[3]

BY FRANCIS C. PHILLIPS.

Received September 9, 1895.

THIS method is based upon the assumption that when iron is dissolved in an acid any sulphur that may occur in the iron unites with the escaping hydrogen, forming hydrogen sulphide. In the usual mode of conducting the process the impure hydrogen evolved is led into a suitable absorbent and the sulphur finally determined, either by oxidation and precipitation as barium sulphate, or by a volumetric method. In applying the process Fresenius[4] directs that the iron be dissolved in *dilute* hydrochloric acid. Von Reis[5] and Blair[6] concur in this recommendation, as does also Dudley in

[1] Monatsh. Chem., 2, 638.

[2] Mr. E. Twitchell of Cincinnati informs us that he has found the glycol present in considerable quantity in the "tank liquor" separating from the fat before saponification.

[3] Read at the Springfield meeting.

[4] Quant. Analyse, *1877*, 428.

[5] Stahl-eisen, *1894*, 963.

[6] Chemical analysis of Iron, p. 54.

the published directions for the determination of sulphur in cast-iron, issued by the Pennsylvania Railroad Company.

For the absorption of the hydrogen sulphide various reagents have been recommended. Johnson[1] proposed the use of a bromine solution. Blair absorbs the hydrogen sulphide in an alkaline solution of lead acetate, oxidizes the resulting lead sulphide, and precipitates the sulphuric acid as barium sulphate. According to the usage at many iron works the gases are led into an ammoniacal cadmium chloride solution which is afterwards acidulated and the sulphur determined volumetrically by standard iodine. In order to complete the expulsion of the hydrogen sulphide from the solution of ferrous chloride a stream of carbon dioxide has been generally employed. Blair uses for this purpose a current of hydrogen, while Dudley states that neither gas has any advantages over air used in a slow stream. In iron-works laboratories it is a generally recognized fact that in the use of the evolution method for certain cast-irons, notably those containing a high percentage of combined carbon, an error is liable to occur, and in cases where great accuracy is required the aqua regia method is usually preferred.

It is common to find that during the solution of cast-iron in an acid there is produced a considerable quantity of strong smelling gaseous hydrocarbons. The interior surface of the flask becomes coated with minute drops of an oily liquid which adheres to the glass and is not miscible with water. There can be little doubt that the loss of sulphur which often results in its determination by the evolution method is dependent largely upon the formation of these organic compounds during the solution of the iron.

It is common to find that the white irons dissolve in acid leaving a nearly white silicious residue of a somewhat flocculent character. This residue contains a varying amount of sulphur, which is insufficient, however, to account for the low results sometimes obtained in the determination.

It has been attempted to explain the error on the hypothesis that sulphur exists in iron in more than one modification, that that portion of the sulphur which occurs in the ordinary form

[1] *Ztschr. anal. Chem., 1874.*

passes readily into hydrogen sulphide on its elimination from the iron by the action of the hydrochloric acid, while another portion existing in some unknown modification, is not converted into hydrogen sulphide, but remains passively in the residue and is thus lost in the determination.

Such an assumption involves a difficulty. It is not usually considered necessary in order to explain the chemical changes undergone by the elements of a compound to suppose that the atoms of carbon, hydrogen or sulphur exist in the compound in forms different from those in which we know them in other compounds. Of the six hydrogen atoms in alcohol one differs from the others as to its behavior towards oxidizing agents. The supposition that there are two allotropic forms of hydrogen in alcohol would hardly be accepted, however, for it is commonly believed to be the mode of linking of the atoms rather than the occurrence of the elements in allotropic forms in the compound that determines the nature of chemical changes. The fact that a portion only of the sulphur in white cast-iron is liberated as hydrogen sulphide by an acid suggests that the molecule of cast-iron does not contain all its sulphur linked in the same manner. In the present paper I have described some experiments undertaken in order to study the reactions of the evolution method more fully. For the purpose in view a white iron containing 0.17 per cent. of sulphur, as found by the aqua regia method was used.

Experiment 1.—Four grams of this iron were dissolved in hydrochloric acid of 1.12 sp. gr. As the process of solution became retarded the acid was heated gradually to the boiling-point. The escaping gas was led into a solution of bromine. A small quantity of a heavy oil collected in the bromine solution. This oil was decanted, introduced into a platinum boat and burnt in a porcelain tube in a current of nitrous oxide gas. The gas escaping from the tube was led into bromine water, which on treatment with barium chloride in the usual way yielded a precipitate of barium sulphate, showing that the original oil had contained sulphur.

Experiment 2.—The oil collected in an experiment similar to the preceding was digested with concentrated nitric acid. The

mixture, contained in a glass-stoppered bottle, was kept at a temperature of 100° C. for two hours. On one evaporation to dryness, re-solution of the residue in water, and addition of barium chloride no precipitation occurred. The solution was then evaporated again to dryness with addition of some barium nitrate, and the residue heated to redness. On re-solution in water a precipitate of barium sulphate appeared. This experiment showed that the oil contained sulphur but in a form not easily oxidizable directly to sulphuric acid by bromine water or concentrated nitric acid. The fact that a precipitate of barium sulphate was not obtained by mere evaporation with strong nitric acid, but was quickly produced on ignition of the evaporated residue and re-solution in water, indicated the possible presence of a sulphur ether of the type $(CH_3)_2S$.

Experiment 3.—That the oil condensed in the bromine flask was not a pure sulphur compound was evident from the following experiment: A few drops of the oil were warmed in a flask with an alcoholic solution of potassium hydroxide. The escaping gas was found to yield a red precipitate in an ammoniacal solution of cuprous chloride, indicating acetylene. From this it seemed probable that the oil found in the bromine solution consisted mainly of ethylene dibromide, which on treatment with the alcoholic potash had yielded acetylene by the reaction

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O.$$

Experiment 4.—The flask which had been used for a sulphur determination by the evolution method, and which exhibited minute oil drops on its inner sides, was rinsed with alcohol and with chloroform. The combined liquids were evaporated in a platinum boat in which a minute quantity of a residue was left. On strongly heating in nitrous oxide and passing the products into bromine water a precipitate of barium sulphate was obtained after the usual treatment with barium chloride.

Experiment 5.—The silicious residue left from the solution of the iron in hydrochloric acid in the determination of sulphur by the evolution method was found on fusion with alkaline carbonate and nitrate to yield a small quantity of barium sulphate when treated in the usual manner for the determination of sul-

phuric acid. It seemed still to be of importance to ascertain whether the sulphur in this residue existed as a metallic sulphide or as an organic compound. The possibility of the presence of free sulphur seemed to be excluded, inasmuch as air had been expelled from the flask during the solution of the iron by a stream of carbon dioxide. Accordingly, the silicious residue from a sulphur determination was dried at a gentle heat and extracted after the fashion of an ordinary fat extraction process by boiling alcohol and afterwards by boiling chloroform. The extract, on evaporation, left a trace of a yellow oil. This oil, on being burnt in nitrous oxide, gave indications of the presence of sulphur when tested in the manner already described.

The silicious residue, after extracting with alcohol and chloroform, was found, on fusion with alkaline carbonate and separation of the silica, not to contain sulphur. From this it appeared that the silicious residue contained an organic sulphur compound, but did not contain a metallic sulphide.

The acid solution of ferrous chloride left in the evolution flask was filtered, agitated with a few cc. of chloroform. The chloroform on evaporation, ignition of the residue in nitrous oxide, and the usual treatment, was shown to contain sulphur.

The following determinations were made in the manner indicated. The percentages of sulphur are based upon the weight of the iron dissolved.

	Per cent.
1. Sulphur from oil collected in bromine solution	0.008
2. Sulphur obtained from alcohol and chloroform rinsings of flask	0.010
3. Sulphur extracted from silicious residue	0.013
4. Sulphur obtained by *fusion* of silicious residue after extracting by alcohol and chloroform	0.000
5. Sulphur obtained by agitation of the filtered ferrous chloride solution with chloroform, representing therefore organic sulphur compounds held in solution	0.009
Total	0.040

This total represents sulphur occurring in difficultly volatile organic compounds and does not include that which is evolved in more volatile compounds. It is not impossible that a loss by

volatization occured in evaporating the chloroform extracts preparatory to combustion in nitrous oxide. It seemed very desirable to learn more of the nature of these organic sulphur compounds and accordingly the following experiment was tried with a larger quantity of iron.

Experiment 6. One thousand grams of the same white iron as had been used in the preceding experiments were treated in small portions at a time with hydrochloric acid of 1.15 sp. gr. until the solution was complete. To hasten the process, as the action of the acid became slow, the flask was gently warmed. The escaping gas was passed, first, through a solution of lead acetate supersaturated with sodium hydroxide, and secondly, through a solution of mercuric chloride in alcohol.

1. THE ALKALINE LEAD ACETATE SOLUTION.

In addition to the deposit of lead sulphide which formed in the lead solution, a yellow flocculent precipitate appeared, soluble on shaking in the alkaline fluid. The solution, decanted from the lead sulphide, was slightly acidulated and warmed. The gas produced was found to yield the following reactions with the solutions named:

Ammoniacal cadmium chloride yielded a white flocculent precipitate.

Palladium chloride yielded a cinnamon colored precipitate.

Platinum chloride yielded a yellowish brown precipitate.

Ammoniacal silver nitrate yielded a pale yellow precipitate.

These reactions indicated the presence of a mercaptan. To study the subject more fully the yellow precipitate, produced in a solution of silver nitrate containing an excess of sodium acetate, was subjected to a partial analysis with the following results:

Found.		Calculated for silver mercaptide.	
Silver.	Sulphur.	Silver.	Sulphur.
69.40	20.54	69.63	20.68

From the data so obtained it appears that methyl hydrosulphide was contained in the gas evolved during the solution of the iron in the hydrochloric acid.

2. THE ALCOHOLIC SOLUTION OF MERCURIC CHLORIDE.

This was found to contain a small quantity of a white precipi-

tate which was partly soluble on warming. After cooling again the solution yielded transparent colorless crystals recognized under the microscope as having the form of crystals of the compound $(CH_3)_2SHgCl_2$ which results when methyl sulphide is added to a solution of mercuric chloride. Upon boiling the aqueous solution of the precipitate in the mercuric chloride solution and leading the vapors into palladium chloride solution, orange crystals were obtained which under the microscope were not distinguishable from the compound formed when palladium chloride and methyl sulphide are brought together. The precipitates formed in the solutions of mercuric chloride and palladium chloride being somewhat soluble, the quantity obtained was insufficient for analysis. It is however very probable that methyl sulphide $(CH_3)_2S$ occurred among the gases evolved during the solution of the iron.

It seems important that in the evolution method of sulphur determination the possibility of the presence of these and kindred sulphur compounds should be taken into account. Two modes of procedure suggest themselves for the recovery of that portion of the sulphur which is liable to be lost in the determination.

I. By direct oxidation to sulphuric acid.

II. By convertion into hydrogen sulphide followed by oxidation to sulphuric acid.

I. DIRECT OXIDATION OF ORGANIC SULPHUR COMPOUNDS.

The action of concentrated nitric acid, potassium permanganate and other energetic oxidizing agents in solution tends merely to convert methyl sulphide into its oxides $(CH_3)_2SO$. and $(CH_3)_2SO_2$. Bromine enters into direct union forming $(CH_3)_2SBr_2$.

Under strongly oxidizing influences methyl hydrosulphide merely yields methylsulphonic acid, an acid which is well known to form a soluble and stable barium salt. Hence while it is a characteristic property of hydrogen sulphide to undergo oxidation to sulphuric acid readily, it is equally characteristic of these organic sulphur compounds and their homologues not to change easily into sulphuric acid even under apparently favorable conditions.

It seemed possible that by direct combustion of the gases the complete oxidation of the sulphur to sulphuric acid might be effected.

A great many experiments have been tried in this direction of which the following is a summary.

As the gases are not evolved in sufficient quantity during the solution of the iron to burn steadily from a jet, it was found necessary to conduct through the evolution flask a current of some combustible gas in order to maintain a more constant flame. For this purpose carbon monoxide was used. The gas was burned from a platinum jet in a glass globe through which a current of moist nitrous oxide was caused to flow. Nitrous oxide was used rather than air or oxygen for the reason that during the combustion of any gas in it nitrogen dioxide is continually formed in considerable quantity. The conditions are therefore highly favorable to the oxidation of any sulphur dioxide produced from the flame of the burning gas, and the complete condensation of the resulting sulphuric acid.

The results were not satisfactory for two reasons:

1. It was found impossible to prevent the occasional extinguishing of the flame, due to the slight pulsations in the gas stream.

2. It was not possible to expel all of the less volatile hydrocarbon oils from the evolution flask into the combustion globe without boiling the ferrous chloride solution and consequent risk of driving over too much steam which tended to extinguish the flame. These difficulties necessitated the abandonment of the method.

II. CONVERSION OF ORGANIC SULPHUR COMPOUNDS INTO HYDROGEN SULPHIDE.

The precipitates produced by the mercaptans in solutions of metallic salts, are not easily converted into sulphides. From this statement must be partially excepted the lead, silver and copper compounds which may change slowly into sulphides. The cadmium compound, which is often seen as a white precipitate when in the evolution method ammoniacal cadmium chloride is used as an absorbent, is more stable. The white precipitate gradually changes into yellow cadmium sulphide, especially on exposure to light.

The process adopted by Blair—absorption in alkaline lead solution—no doubt possesses an advantage on account of the possible change of the lead compound into lead sulphide, as it in this way may affect the recovery of a portion of the lost sulphur. The compounds of the sulphur ethers of the type $HgCl_2(CH_3)_2S$ are still less prone to change into metallic sulphides under the conditions imposed by the method.

Experiment 7.—The vapor of methyl sulphide largely diluted with carbon dioxide was passed through a red hot porcelain tube. By this treatment the sulphur compound was shown to be readily convertible into hydrogen sulphide, undergoing, however, an intermediate transformation into methyl hydrosulphide, CH_3SH, a gas which is easily recognized by its reactions with various metallic salts in solution.

Based upon the results of these experiments the following modification of the evolution method was tried:

The iron was dissolved in hydrochloric acid of 1.12 sp. gr. added slowly while a stream of carbon dioxide was being transmitted through the flask. Heat was applied as soon as the action became retarded. The escaping gas was led through a porcelain combustion tube heated to dull redness. The porcelain tube contained a roll of platinum foil eight inches long. The delivery tube from the evolution flask was pushed far enough into the porcelain tube to permit any liquid which might distil over to drop into the hot platinum roll. A slow stream of carbon dioxide was passed continuously through the evolution flask and heated porcelain tube. The solution of the ferrous chloride was finally heated to gentle boiling and kept boiling until the oily drops which usually coat the sides of the flask were carried away. This required two hour's boiling or two and one-half hours for the entire process. Inasmuch as organic compounds of high boiling-point are undoubtedly formed, this long-continued boiling is especially important. As an absorbent, bromine dissolved in dilute hydrochloric acid was used. After passing a nitrogen flask containing the bromine solution the gas was conducted to the bottom of an eight liter bottle containing a little of the same bromine solution. Experiments have shown that the use of this large bottle is necessary to the complete con-

densation of the sulphuric acid. The platinum foil used in the porcelain tube is not essential but protects the porcelain tube from risk of fracture from the dropping of the liquid upon its heated inner surface. Mica may be used instead of platinum but is rapidly corroded by the hot acid vapors. The sulphur was determined by weighing as barium sulphate.

In the following table column II contains the results of some determinations of sulphur by the method described.

Column I contains results obtained by the same method except that no heated tube was used.

Column III contains results obtained by the aqua regia method as described by Blair.[1]

The irons used for the determinations were selected on account of their high percentage of sulphur.

Evolution method. Per cent.	Evolution method. Gases passed through a heated tube. Per cent.	Aqua regia method of Blair. Per cent.
	IRON A.	
0.059	0.096	0.101
0.046	0.095	0.098
0.050	0.104	0.096
0.050	0.104	0.099
0.054	0.099	0.100
0.055	0.100	0.102
....	0.092	0.102
....	0.105	0.104
....	0.098	....
....	0.101	....
Mean 0.052	0.099	0.100
	IRON B.	
0.100	0.183	0.173
0.101	0.178	0.170
0.087	0.175	0.168
0.099	0.181	0.170
0.092	0.177	0.174
0.084	0.188	0.171
Mean 0.094	0.180	0.171

In conclusion, I have to thank Messrs. F. B. Smith and H. C. Beggs for the very great care they have taken in carrying out the determinations by the method described.

[1] Chemical Analysis of Iron, p. 57.

ON THE VOLUMETRIC DETERMINATION OF LEAD.

By Allerton S. Cushman and J. Hayes-Campbell.

Received September 26, 1895.

FRESENIUS in the last edition of his Quantitative Analysis commenting on the volumetric determination of lead, says: "Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz,[1] briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator owing to the yellow color of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle[2] modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow color of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow color gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavor to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardized solution of ammonio ferrous sulphate, using potassium ferricyanide as an outside indicator under exactly the same conditions observed in standardizing bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardized against a weighed amount of pure dried ammonio ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then

[1] Dingl. poly. Jour., 169, 284.
[2] *Ztschr. anal. Chem.*, *1880*, 306.

weighed out and dissolved in a liter of water with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a siphon tube and pinchcock so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio ferrous sulphate solution takes place very slowly, while as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well mixed sample of a crystallized galena containing only a little silica as impurity was first analyzed by the method of Rose as given in Fresenius, Quantitative Analysis. The lead is precipitated as the sulphide, with the proper precautions, the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained :

No.	Weight taken. Grams.	Weight lead sulphide. Grams.	Lead sulphide. Per cent.	Lead. Per cent.
1	2.0000	1.9870	99.35	86.08
2	2.0000	1.9856	99.28	86.00
3	1.9988	1.9856	99.35	86.06

The next series of results were obtained by the method of Albert H. Low.[1] Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried and weighed. By this method the following results were obtained :

No.	Weight taken. Grams.	Weight lead. Grams.	Lead. Per cent.
1	0.5000	0.4341	86.82
2	0.5013	0.4311	86.00
3	0.4972	0.4313	86.64
4	0.5025	0.4371	86.98
5	0.5019	0.4351	86.25
6	0.5223	0.4540	86.92

[1] *J. Anal. Appl. Chem.*, **6**, 12.

These figures show a general tendency to high results which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's[1] modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands and the percentages found were invariably low. As the method did not present any advantage over others either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows: About one gram of finely pulverized ore is digested in a casserole or evaporating dish with fifteen cc. of a mixture of two parts nitric and one part sulphuric acid until decomposition is complete. Ten cc. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with ten cc. of dilute sulphuric acid (1–10) and then add gradually forty cc. of water. Heat to boiling, filter and wash by decantation with dilute sulphuric acid (1–10) getting as little of the lead sulphate on the filter as possible. To the residue in the dish add twenty cc. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow color. Allow to settle for a few minutes then filter, under pressure if possible, wash a few times and titrate the filtrate against the standard ammonio ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be

[1] *J. Anal. Appl. Chem.*, 6, 11.

free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution, the acid is neutralized with an excess of ammonia and then made acid with acetic acid; this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:

No.	Weight taken. Grams.	Calculated weight lead found. Grams.	Lead per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
6	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.

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REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID.[1]

BY CHAS. BASKERVILLE.
Received September 9, 1895.

ANDREWS[2] in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary pro-

[1] Read at the Springfield meeting.

[2] Chem. News, 70, 152.; Iowa Acad. of Sciences, Proc. p. 4.

duct. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction so simply treated in most text-books.

When my work was completed, in verifying my references I chanced on Pickering's[1] work on the same subject which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Prof. Pickering. My observations concerning the primary reactions were not the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

Primary:

$$(1)\quad Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

This may be regarded as taking place in two steps:

$$(a)\quad Cu + H_2SO_4 = CuSO_4 + H_2,$$
$$(b)\quad H_2 + H_2SO_4 = SO_2 + 4H_2O.$$

Still no hydrogen could be detected in the gas given off.

$$(2)\quad 5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O.$$

Secondary:

$$(1)\quad Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O.$$
$$(2)\quad CuS + 2H_2SO_4 = CuSO_4 + S + SO_2 + 2H_2O.$$

The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated C. P. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide

[1] J. Lond. Chem. Soc. Trans., *1878*, p. 112.

and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experiment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper as sulphate was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue treating with carbon disulphide and the loss in weight taken as sulphur.

Primary Reactions.—My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures (0°–270° C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occured. The proportion of the material following the second equation increased from 0° to 100° C., and then decreased to 270° C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under 100° C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from 100° to 130° C. as may be seen from the table. The proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at 270° C. and lasts for only a few seconds.

No.	Temperature of reaction.	Copper used.	Copper as sulphate.	Copper as sulphide.	Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°–10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°–30°	1.3379	1.3260	0.0121	....	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0.1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°–80°	0.0760	0.0730	0.0035	....	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°–130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°–160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°–190°	1.1375	1.1200	0.0930	....	12.0 : 1
13	200°–220°	1.5450	1.4518	0.0932	1.0904	16.0 : 1
14	220°–230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°–260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	....	None.	....	....

Berzelius[1] noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel[2] found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming copper sulphide and oxide, the latter being dissolved in the acid.

Maumené[3] claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides, $CuO.2Cu_2S$ or $Cu_5S_2O_,$, $CuO.2CuS$ or Cu_3S_2O, and $CuO.CuS$ or Cu_2SO.

In my analyses, as also in Pickering's, the sum of the percent-

[1] Traité de chimie, 4, 324.

[2] Journ. de Pharm. 20, 13, *1834*.

[3] Ann. Chim. Phys., *1846*, 3rd Series, 18, 311; Traité de chimie générale, Pelouze et Fremy, 2nd Ed., I. 388.

ages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated $CuO2Cu_2S$. I shall speak of that apparent exception further on.

Calvert and Johnson[1] performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from 130° to 150° C. They noted the formation of the subsulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.[2] There was evidently something very wrong in their observations, for they failed to note any action below 130° C. Barruel in 1834 had noted that action took place at the temperature of the air. I have noted the action at 0° C.

According to Andrews

$$Cu + SO_3 = CuO + SO_2$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

are the correct formulas, SO_3 existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at 0° C. Besides this the undissolved residue is not the oxide at all, as he says it is, but invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I have learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.		Calculated for Cu_2S.
Sulphur	20.44		20.14
Copper	79.56	(by difference)	79.86
	100.00		100.00

In the first of the two primary reactions,

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O,$$

[1] J. Chem. Soc., **19**, 438, *1866*.

[2] Pickering proved this impossible. The amouut of sulphide produced was not increased by adding sulphur direct to the experiment.

it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved. Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as sulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula

$$5Cu + 4H_2SO_4 = 3CuSO_4 + Cu_2S + 4H_2O$$

shows that relation between the two compounds of copper.[1]

Secondary Reactions.—The secondary reactions depend upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150° C when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59.[2]

[1] Pickering states (*loc. cit.*, p 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2 : 2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

[2] Watts (vol. II, p. 41, *1875*, Ed.) notes this complete decomposition.

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur	32.36	33.59

The formula,

$$Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + H_2O$$

explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur	19.71	20.138

The formula

$$Cu_2S + 4H_2SO_4 = 2CuSO_4 + 2SO_2 + S + 4H_2O$$

shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1. $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O$.
2. $CuS + 2H_2SO_4 = S + CuSO_4 + SO_2 + 2H_2O$.

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons:

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.

2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.

3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.

4. If flowers of sulphur be heated with concentrated sulphuric

acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated $CuO.2Cu_2S$ in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to 250° C. in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis:

	Found.	Calculated for $CuO.2Cu_2S$.
Sulphur	16.16	16.15
Oxygen	3.54	4.03
Copper	undetermined	79.82

Schuster[1] found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube[2] noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for SO_4 and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being:

$$Cu + H_2SO_4 + O = CuSO_4 + H_2O_2,$$

and

$$Cu\,H_2O_2 = CuO + H_2O.$$

I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen peroxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering[3] sug-

[1] Proc. Roy. Soc., 55, 84; *Ber. d. chem. Ges.*, **28**, 219.

[2] *Ber. d. chem. Ges.*, **18**, *1887–1890*.

[3] *Loc. cit.*, p. 138.

gests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

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NEW BOOKS.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. By HARVEY W. WILEY. Volume I, Soils. Cloth, 8 vo., pp. 607, figures, 93. Easton: Chemical Publishing Co. 1894. Price, $3.75.

This first bound volume includes the first eight parts of the compendious work now in process of publication.

In attempting to meet the wants alike of analysts, teachers, and students of agricultural chemistry, the author has undertaken a most difficult task. The needs of the several classes of readers are widely different, often distinctly opposite.

Beyond doubt, each of the classes named has need of a thoroughly modern treatise upon this subject. There is extant no satisfactory systematic introduction through the general principles of analysis to the special methods applicable to agricultural materials; the student is ordinarily compelled to the study of many methods, in the illustration of general principles and for the acquirement of facility in manipulation, that are not directly required in his future work, and which might often be happily substituted by methods which are of immediate use. Again, there is no English work on agricultural analysis—except of the most incomplete scope—which is at all modern; nor does any work upon the subject in any language cover the methods developed in America during the past ten years. On the other side, the Proceedings of the Association of Official Agricultural Chemists state the American official methods most briefly, for the guidance of analysts presumably acquainted with the methods in general, and more or less familiar with the reasons for the several specifications, and, therefore, without explanatory comment; nor has this Association undertaken, as yet, to cover all of the large field involved. Even assuming a degree of linguistic attainment altogether beyond that of the average student, and of

many a practicing analyst, the foreign treatises upon the subject are often so brief as to mislead the student and to be useless even to the practicing analyst. The opening for a treatise of the design outlined by Professor Wiley is therefore wide.

The perspective of the volume will serve quite well, perhaps, to elucidate the author's treatment of his subject in its salient features; of 607 pages, over one-tenth is devoted to a brief study of the materials to be analyzed, and their origin; one-twentieth is given to the sampling of the soil; one-seventh to the physical properties of the soil, including their estimation; one-sixth to mechanical and mineralogical analysis; one-thirtieth to the determination of the gases of the soil; the remaining half of the volume deals with the chemical analysis of the soil, including soil waters.

In no other treatise of this kind are the relations of the analytical method to the nature of the problem it is used to solve, so fully dwelt upon; and in no other similar treatise do the physical and mineralogical properties receive a treatment so fully in accord with their importance.

The style is clear and compact. In his selection of methods no attempt has been made by the author to limit those described to the number found useful in a single laboratory only, but general experience has rather been consulted. Especial stress is laid upon American methods because the reader will chiefly use these methods, and because other treatises so frequently ignore them; yet no other treatise gives nearly as full discussion even to the Continental official methods, and the judicial impartiality of the author is highly praiseworthy. The very recent literature has been drawn upon for material, and the wealth of reference will be especially appreciated by the teacher and analyst; this volume alone contains 348 listed references to original papers.

This work is furthermore noteworthy as being probably the first important chemical treatise to rigidly follow the American Association for the Advancement of Science revision of chemical orthography. The practice of beginning with a lower-case type all proper names used in the text to designate methods is an innovation less certain to be followed. The figures are well selected and apposite.

The publishers are to be congratulated on the beautiful typography of the volume, its good press-work, and its freedom from printer's errors.

Judging of this work by the first volume it may be said, briefly, that it is the most modern, the most complete and the very best treatise upon the subject of agricultural analysis, and that it meets more largely than any other book on the subject, the needs of the teacher, the student, and the working analyst. It is not, of course, a text-book of agricultural chemical analysis, nor a hand-book of the laboratory, but it should find its place upon the reference tables of all laboratories. Nor is its usefulness confined to the analyst of agricultural products alone, for every general analyst will find in its pages a great mass of material, superbly arranged, to which he could daily refer with direct advantage to his work. WILLIAM FREAR.

A HAND-BOOK OF INDUSTRIAL ORGANIC CHEMISTRY. By SAMUEL P. SADTLER, PH.D., F.C.S. Second revised and enlarged edition. 8 vo. pp. 537. Philadelphia: J. B. Lippincott & Co. 1895. Price, cloth $5.00, sheep $6.00.

The hundreds of manufacturers of chemical products in this and other countries who are struggling with the puzzling problems of daily practice and the vexatious details so essential to commercial success, eagerly watch for and greedily accept everything which may possibly clear up difficulties or offer suggestions, and such works as this of Dr. Sadtler's find the heartiest of welcomes waiting for them. It is not surprising, therefore, that this work from so excellent authority should soon be out of print and that a second edition should be needed to meet the current demand.

Limited in volume, and, therefore, in detail, works of this class serve two important purposes: First, they furnish teachers in compact and reliable form for presentation to their students, ample description of the principles and processes used in the chemical industries. Second, they furnish manufacturers, working in more or less empirical ways, knowledge of the fundamental principles of the processes they employ, or general principles of methods other than their own but attaining the same end, possibly with greater economy both of time and means.

In the second instance they meet only partially the prevailing

demand. Manufacturers are desirous, it is true, of becoming acquainted with the experience of others even in other branches of industry. but the difficulties they meet are frequently, if not generally, as much mechanical as chemical, and better and more effective forms of apparatus as well as general reactions are needed. Furthermore, profits in manufacture depend in these days largely upon the utilization of the waste products, and the practical operation of many processes are dependent upon the retention or destruction of wastes, noxious or undesirable. Methods and apparatus are wanted for properly caring for these important factors of the industrial problems.

In the work before us Dr. Sadtler has succinctly set forth the progress attained to date in the industries discussed and in a large measure has met the demands described. Perfection is rare, and doubtless many of us might be able to suggest additions to the several chapters dictated by personal experience; yet with the material offered, together with the bibliography, the references to other and larger works and particularly to the periodical liturature, it is questionable if one can find a better time saver in all the range of technical-chemical publications than is provided in this work.

In fourteen chapters, covering 492 pages, the industries most common to this country, at least, are discussed under five general heads, *viz*: Raw materials; Processes of manufacture; Products; Analytical tests and methods; Bibliography and statistics; and in this systematic way the essential facts are presented. Descriptions for empirical work are accompanied by analytical methods for rational control. In addition thereto is an appendix giving conversion tables and tables of physical and chemical constants useful wherever the work may go.

One hundred and twenty-seven most excellent cuts representing machinery and apparatus used in the works or laboratories illustrate the text and fourteen diagrams illustrate the various successive steps in processes of manufacture or analysis. A thoroughly complete index makes reference most convenient and will charm those who have suffered the vexation incident to the use of books not similarly provided.

WILLIAM MCMURTRIE.

BOOKS RECEIVED:

On the Densities of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights. By Edward W. Morley, Ph.D. City of Washington, published by the Smithsonian Institution, 1895. 4°. xi, 117 pp. Price $1.00.

From Smithsonian Contributions to Knowledge, Vol. XXIX. (Number 980.)

The Scientific Foundations of Analytical Chemistry. By Wilhelm Ostwald, Ph.D. Translated by George M'Gowan, Ph.D. New York, published by Macmillan & Co., 1895. 8°. xviii, 207 pp. Price $1.60.

Organic Chemistry. The Fatty Compounds. By R. Lloyd Whiteley, F.I.C., F.C.S. New York, published by Longmans, Green & Co., 1895. 8°. viii, 291 pp. Price $1.00.

A Manual of Qualitative Chemical Analysis. By E. P. Harris, Ph.D., LL.D. New edition, revised. Amherst, Mass., printed by Carpenter & Morehouse. 8°. 315 pp. Price $1.50.

Maps of British Columbia, Nova Scotia, Quebec and Ontario. Ottawa, the Geological Survey of Canada. 1895.

Practical Proofs of Chemical Laws. By Vaughan Cornish, M. Sc. London and New York, published by Longmans, Green & Co., 1895. xii, 92 pp. Price 75 cents.